Modern Molecular Thermodynamics (Physical Chemistry 1)

Open Educational Resources

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How to Use this Book?

The author has provided 23 chapters on specific topics of Chemical Thermodynamics, beginning with the Kinetic Theory of Gases. The book builds gradually on fundamental concepts and relates them to molecular properties of substances, in unique ways, and hence the title, ‘Molecular Thermodynamics’. Another unique feature of the book is bringing the deep concepts of thermodynamics to our everyday experiences. This is done via self-reflection studies where the student is asked to examine their dorm room to find answers, moving classroom to the dorm room. In addition, each chapter also has a good number of worked out numerical problems for the student to train their skills in physical chemistry. Author suggests working through all the worked out examples in each chapter, followed by solving the puzzles given under the self-study exercises, Self Tests and finally the numerical problems.

Dedication

This free textbook is dedicated to my loving parents, (late) Mrs. Challa Mytreyamma and Dr. Challa Venkatarama Serma, my awesome wife Anupam Kumar and to my early mentors Professor K. Akshayakumar and Mr. K. Ksheera Sagaram.

Acknowledgements

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Chapter 1. Introductory Mathematics

After completing this chapter, you will be able to:

- Recognize the linear functions, trigonometric and exponential functions.
- Graph certain functions along the cartesian coordinate system.
- Apply differentiation to evaluate first and higher derivatives, recognize the relation between the derivative and the tangent.
- Evaluate the relation between differentials and rates of changes of physical quantities with respect to other key parameters.
- Identify the area under the curve with the integral of the function within set limits and recognize some differentials.
- Examine the examples of everyday events that involve first and higher order derivatives.
- Recognize the physical significance of specific mathematical functions and their interpretation in terms of daily experiences.

Goals

- Review several key mathematical concepts that are routinely used in this book and refresh the memory of the reader on these topics.
- Briefly survey certain mathematical functions, plotting of graphs, differentiation, partial differentiation, and integration.
- Examine the behavior of functions, their limiting values, slope of the function at some specific point (differentiation), value of maxima or minima, area under the function over an interval (integration) or assess the value of the function within specific boundary conditions or limiting values.
- Search the physical meaning or the interpretations of the functions or their properties under specific sets of conditions.
- Recognize examples of mathematical functions and operations in day-to-day events to bolster our understanding of abstract concepts with concrete examples.

1.1 Why Study this?

This chapter is not meant to teach the required mathematics to successfully follow this book, but it is intended to prompt the reader some of the salient features that they already learned in pre-requisite courses leading up to this point. Certain specific items that the reader may have to look up in their notes from algebra and calculus courses will be pointed out, and certain relevant examples will be presented here. There is more to this discussion than what will be presented here. This extra piece needs to be filled in by the reader.[1]

The items that the reader would like to review to refresh their memory of earlier math courses are the following: differentiation and integration of certain functions that are routinely encountered in this book. For example, we will be dealing with exponential functions, log functions, linear functions, quadratic functions, polynomials, trigonometric functions, factorials, permutations and combinations, simple series, and summations of series. Familiarity with the properties of these will be greatly useful for discussions of the subject matter provided in this book. Thus, we need to be proficient in certain math concepts to make sense of the contents of this book. There are numerous open educational resources available to supplement current discussion.[2,3,4] This discussion is further continued in the following section.

1.2 What's with Physical Chemistry and Math?

Why do we need to use math in physical chemistry in the first place? Can't we do this discussion by simply saying this quantity is greater or lesser than that other quantity or this equation works this way, or works the other way? In other words, can we not deal with some qualitative descriptions of these equations, instead? Why do we need to be quantitative? The answer to this dilemma is a bit long but simple, as detailed below.

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[1] http://libguides.humboldt.edu/openedu/math
[2] http://irsc.libguides.com/mathematics/OER
[3] http://guides.ou.edu/OER/mathematics
[4] https://nmc.libguides.com/oer/math

Physical chemistry is said to be an amalgam of physics, chemistry, and mathematics, and in the words of a colleague of mine, it is "algebra written in a foreign language." However, it need not be that way. We will try and relate concepts of physical chemistry with our day-to-day experiences so that one can relate to these concepts and understand them much better. This is where the quantitative descriptions are essential to predict specific outcomes of a given set of processes. Although physical chemistry has this flair of abstractness it is a description of down-to-earth experiences, which are based on chemistry and/or physics.

1.2.1 Changes in a System

In this book, we will be examining changes in the properties of our system, this latter word will be defined more precisely in subsequent chapters, but for now, consider this as a specific region of the universe that is of immediate interest to us. Changes in properties of the system are best described by calculus and it will guide us through the quantitative aspects of physical chemistry. Thus, oftentimes "change" is what we are interested in. Even when the change is not apparent, as, in the case of chemical equilibrium, there are changes taking place. To maintain the equilibrium, these changes are taking place in opposite directions, in equal measures so that the net change in the system is zero, and hence the system is said to be at equilibrium. Our inquiry will be about changes that are happening in the system and how we can predict what changes the system will undergo. For example, we might ask will a chemical reaction move forward, go back or stall when we change a specific property of the system such as temperature. We can answer this question by constructing mathematical functions that describe specific properties of the system, and we take derivatives of this quantity as a function of another property of interest. Then, the derivative tells us how the energy of the system changes when we change one of these other properties of the system.

For example, we might ask how does the energy of a system change with temperature, under a specific set of conditions? The precise answer lies in constructing and evaluating the first derivative of energy with temperature under specific conditions, such as in a constant volume process, for example. Thus, we need specific quantities or functions of quantities and differential calculus to answer this type of question in quantitative terms.

The following is an example of a change in a chemical process. When a chemical reaction is occurring, the concentrations of the reactants and products are changing as a function of time, and this falls under the study of chemical kinetics. If we need to know the rate of the reaction with respect to any one of the reactants or products, we need to know the first derivative of the concentration of that species, as a function of time, among other information. Thus, differential calculus is of prime importance in estimating or measuring changes in the properties of the system.

In other circumstances, we might use integral calculus to estimate the magnitudes of changes in a property over a specified interval of change of that property. That is, we might ask what is the work done in a process when the volume changes from an initial value to a final value, under a well-defined set of conditions? If this given process is a reversible one (this process will be defined in later chapters), then we will use integral calculus to arrive at an estimate of the work for this process over the specified interval. Thus, integral calculus is of importance here. Thus, if we are interested in changes occurring in our system, we must use calculus in one form or another, and thus, calculus is of high significance in chemistry.

1.3 Mathematical Functions for Modeling Chemical/Physical Processes

In another context, we will build mathematical models to define a new property of our system in terms of experimental parameters of interest. This kind of modeling often involves certain mathematical transformations of functions that we already know and build new functions that describe the property of interest. For example, we may know how the pressure of a gas sample depends on volume at constant temperature and constant gas mass (Boyle’s law). Also, we might know how the volume depends on the temperature at constant pressure and constant gas mass (Charles’ law). Both are described by their corresponding mathematical equations that we will examine in subsequent chapters. Next, we might want to construct a new function that connects all the four above attributes of our gas sample, that is pressure, volume, temperature, and mass by a single equation. In other words, we may obtain a deeper understanding of the gas behavior if we were to combine two or more functions into a single equation. And from this combined equation, we can simplify the evaluation of changes during a process that our gas sample undergoes and make precise conclusions, deductions, and even extraordinary predictions. This is because mathematics is a powerful tool and when applied correctly it can tell us attributes that we might have never even imagined or succinctly explain large quantities of data. This is the reason we use quantitative analysis on a mathematical basis to be able to make sense of experimental data as well as numerous day-to-day experiences. This sounds powerful, and it is. Many people might agree with the notion that physical chemistry is an integral combination of common sense and calculus. This may be too profound, but you'll see how this is the case in the discussions presented in the subsequent chapters.

Several equations in physical chemistry use simple mathematical functions. Having said that, we will also encounter many complicated functions but not very often. So, by and large, we will not be dealing with very complicated functions, but we would be able to write derivatives or partial derivatives of simple functions for discussions in thermodynamics. We should be able to integrate certain simple functions with ease. Thus, knowledge regarding certain rudimentary mathematical functions will form a strong foundation for our interpretations and mathematical derivations.

In the following discussions, we will declare x as the independent variable (one that is often controlled in an experiment), while y is the dependent variable which is often measured as a function of the independent variable. This will be the notation in all our discussions where two variables are involved but multi-variable problems will also be encountered in this book. Some of these functions are discussed next.

We will first examine few properties of functions such as linear, quadratic, and exponential functions as well as trigonometric functions. It will be useful to make a list of such functions and their properties for problem-solving. We'll be spending a great deal of time looking at the physical basis or physical meaning of equations that we derive in this book, and we will be deriving equations rather rigorously with specific assumptions and limits. Graphical plots of some of these functions are shown in Figure 1.1.

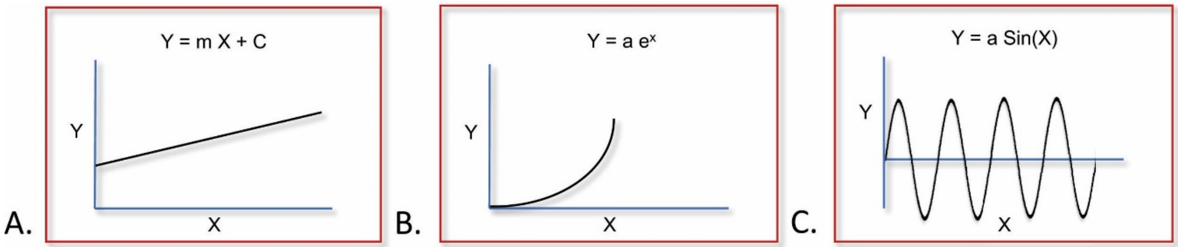

Figure 1.1 Mathematical functions and their plots. A. Linear. B. Exponential. C. Trigonometric.

1.3.1 Linear functions

The equation of a straight line, such as $y = mx + c$ connects any two properties of our gas sample, x, and y. To understand this equation better, we plot y versus x over certain values of x and y, and then estimate the slope (m) and the y-intercept (c). The plot in Fig. 1.1 A is that of a linear function. Plotting a function is important to gain a physical interpretation of the function or the equation that we are interested in. The sign of the slope of the line, 'm' in the above linear equation, will tell us the sign of the change in y with respect to x. The constant 'c' is equal to the value of y when $x=0$, and it is the y-intercept of the linear function.

Example 1.1

If we plot x vs y for a given set of experimental data, and we get a straight line, then we can conclude that we have a linear relationship between the properties of the system, x, and y. From this plot, we can predict what will be the value of y at any value of x, even if it has not been measured directly. Thus, mathematics provides us the ability to predict what would be the outcome if a particular measurement is made. The mathematical equation provides a better understanding of how the properties x and y of the system are related, which may not be obvious from a table of these values.

In addition, we can estimate the slope 'm' and intercept 'c' which are not directly measured in the experiment and not obvious from the table of data. Only after the mathematical analysis of the data collected, followed by the identification of the linear function as the best descriptor of the properties 'x' and 'y', we can arrive at the slope and the intercept values. The slope can be positive, negative, or zero, and this is also true for the intercept. When the slope is positive, then we see that y increases with x, and when the slope is negative the value of y decreases as x increases. Similarly, the intercept can be positive, negative, or zero and defines the value of y when x=0. Sometimes it may not be possible to experiment x=0, for example, then we can predict what would have been the value of y, under these conditions. Thus, mathematical modeling of the experimental data often supplies additional attributes of the system that were not directly measured or sometimes could not be measured readily. This is another major reason to use mathematics in our quest to understand the physical world surrounding us. For our discussions in this book, the reader needs to be able to plot the above graph for a given linear equation, identify values of the slope and the intercept on the y-axis. There are certain apps currently available to do this exercise, but it is very instructive to plot with a pencil on paper and examine the above properties, at least in the case of linear equations.

Occasionally, we will also evaluate the intercept of our linear function on the x-axis. So, the extrapolation of this red line to the left in Figure 1.1 A., top panel, cuts the x-axis on the left at some point. Of course, such an intercept may have a negative value, depending on the location of the y-axis shown in the above graph. That is, we can estimate the value of x when y=0, even when this measurement was not done. Note that the error in measuring the slope is smaller than the error in measuring the intercept because we can see that small changes in the slope can cause much larger changes in the y-intercept.

Example 1.2

In addition to the y-intercept, the x-intercept must also be calculated for a fuller understanding of our linear function, and this can be obtained by the extrapolation of the line in Fig. 1.1 A to the left of the y-axis. We will do this when we discuss Charles' law in the subsequent chapters. However, one needs to keep in mind that our extrapolation should be valid for this value to be accurate. If the function is no longer linear in the region of extrapolation, our prediction will be incorrect or even wrong. Thus, a thorough experimental evaluation of our mathematical function is important for the reliability of the interpretations of the behavior of the system by that function.

1.3.2 Exponential functions

In addition to linear functions, we will also encounter exponential functions, and these often describe many natural processes occurring around us. A simple exponential function like y=a*exp(x) where 'a' is a constant is common in our discussions in this book. For example, all first-order processes are described by this function, and it is an amazing mathematical function in many respects with particularly interesting attributes, some of which are given below.

Example 1.3

A plot of y against x for an exponential function gives the upward bent curve in Figure 1.1 B, middle panel, where y-value increases more and more rapidly as x-value is increasing linearly. This is a positive exponential and describes the growth of a bacterial colony when nutrients are abundant. One characteristic of this function is that the value of y doubles for a specific value of x called the half-life. For example, for each half-life of say, a certain number of hours, the population of a bacterial colony doubles. Thus, if an animal is infected by such a bacterial colony, then things can suddenly take a turn for the worse, and the infection could become lethal quickly, because of this doubling of the bacterial count for each half-life. Therefore, early treatment of a bacterial infection may be critical for a quick recovery from the infection. On a positive note, the simple interest calculated on a savings account in a bank grows exponentially, and thus, most economists recommend saving over a long time as considerable growth of the interest occurs at later times but not in the beginning.

The above example is an exponential growth function, and when the value of y decreases with x, we have a negative exponential function or decaying function, as in a first-order reaction with respect to a reactant. So, the sample may remain radioactive for a long time. Similarly, if the consumption of a reagent in a chemical reaction is first order, then the reaction will never go to completion, strictly speaking. This is because the initial consumption of the reagent might be rapid but strictly speaking it will take infinite time to completely consume the reagent. In practical terms, after a certain reaction time, the concentration of the reagent could be too small to measure and thus, may be considered equal to zero. The reaction will require infinite time to complete. Thus, we can’t truly claim that a given first-order reaction is completed over a finite time, while in principle it will prolong to infinite time.

Example 1.4

Another example is the radioactive decay of elements where the mass of the radioactive element is decreasing exponentially with time. This may be viewed as advantageous because of the rapid initial decrease in the radioactivity of a given sample, decreasing the hazard quickly, but at the same time, we must recognize that radioactivity of the sample will continue for a long time and that it will be truly zero only at infinite time. Thus, exponential functions very are interesting.

1.3.3 Trigonometric functions

A trigonometric function, y = a*sin x where 'a' is a constant, is shown in Figure 1.1 C and we'll be using a few different trigonometric functions in this book, but not all of them. If you plot this trigonometric function, we will see that the value of y is oscillating up and down as we move along the x-axis. As the x-value increases linearly, for example, the y-value initially increases from zero, reaches a maximum, decreases, reaches zero, and becomes negative before recovering back to zero. As we move further along the x-direction, the whole cycle repeats. Thus, we recognize a cyclic relationship that keeps repeating itself as we traverse down the x-axis. The oscillations of a simple pendulum follow a trigonometric function, but it is left to the reader to find out which function it is. We strongly suggest consulting your notes on Trigonometry to refresh your understanding of trigonometric functions.

Along the above line of discussions of functions, we will also be dealing with mathematical series and sums of series. We will provide relevant information in the book when needed, but we strongly urge the reader to consult their notes and textbooks on this important topic.

In addition to the above mathematical concepts, we also will be using the basic theory of probability and probability functions, and this again will not be very intricate or complicated in our discussion, but we're going to deal with probability, particularly when we talk about entropy and statistical interpretations or descriptions of entropy. A basic understanding of probability and probability functions is strongly suggested.

1.4 Differentiation and its Physical Significance

This is a very brief introduction to differentiation and the physical meaning of differentiation of a function, particularly something that we will be using quite often. Let's look at the differentiation of some functions of y and x, shown in Figure 1.2. Let's say that the black curve is the function that we are interested in and if we want the first derivative of this function at any x-value, we can simply get that graphically by drawing a tangent at that point and measuring the slope of the tangent. The slope of the tangent is the first derivative of the function at that specific point, and the slope is negative in this instance (see discussion on linear functions above). Accordingly, the first derivative that we learned to write as dy/dx, which is the ratio of an infinitesimal change in y when an infinitesimal change happens in x. This dy/dx is also the rate of change of y with respect to x, and in graphical terms, it is the slope of the red line. The slope will be zero for the tangent when it is parallel to the x-axis. Now, note that as we draw the tangent at different points on the curve, we will be getting different slopes. As we move along the x-axis, the slope of the tangent (which is negative for x>0) will keep decreasing. Please refer to your math book for a list of the first derivatives of common functions, which will be useful for our discussions.

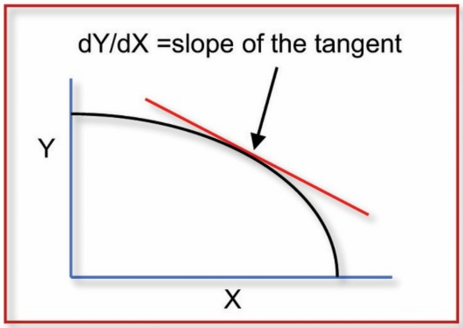

Figure 1.2 Derivative of a function at a particular value of x, indicated as the tangent (red line).

1.4.1 Gas mileage as a first derivative

The slope of the tangent (first derivative) can be related to many quantities that we encounter in day-to-day life. For example, any quantity that changes with respect to a given variable is potentially amenable to first derivative analysis. What does this mean?

Example 1.5

Let's say that you start driving your car from home to school. We can calculate several kinds of derivatives with respect to this process. For example, we can plot the number of gallons of gas consumed by the car on the x-axis and the corresponding distance driven on the y-axis. We can draw tangents to this experimental function at different distances, or values of x, but what does the slope of the tangent tell us? The tangent gives the number of miles traveled per gallon of gas consumed, or the gas mileage as you traveled through the journey, at different points. Remember that this value need not be a constant, because you may have driven uphill or downhill or stopped at a traffic light or sped on a highway. But the point is that gas mileage at any point of your journey is the first derivative, miles traveled per gallon of gas, miles traveled per 1 gallon of gas consumed.

1.4.2 Speed and speed limits as first derivatives

Another popular example for the first derivative is the speed at which you are driving the car. How many miles per hour are you driving? Your speed during the journey from home to school can change and sometimes you go faster but sometimes you may go slower. Therefore, the first derivative of the function of distance vs. time at specific points gives your speed (miles per hour). The car is calculating the first derivative and displaying that value in the speedometer on the dashboard as you drive. When that exceeds the posted speed limit, you might be greeted by a traffic cop with a violation. Thus, the first derivative is the rate of change of y with respect to x, if there is no change, the slope is zero and the tangent is horizontal to the x-axis. Thus, next time when you look at your speedometer or a posted speed limit on the street, think about the first derivative. Pretty cool!

1.4.3 Chemical potential as a first derivative

Chemical potential is one of the quantities that we will use to calculate specific chemical properties. It is simply the first derivative of Gibbs free energy (G) with respect to mole numbers (n), dG/dn. Thus, we can say that chemical potential is free energy per mole of the substance or the rate of change of the free energy with respect to mole numbers. Similarly, heat capacity at constant volume is the first derivative of internal energy with respect to temperature, while the heat capacity at constant pressure is the first derivative of enthalpy with respect to temperature. However, the first derivatives of G or entropy (S) with respect to temperature are not commonly named or used in this book. Density, which is mass per unit volume, is the first derivative of mass with respect to volume. The rate of a chemical reaction is the first derivative of concentration with respect to time. Thus, many first derivatives are encountered in chemistry.

You can find very many examples of calculus in our daily lives where you are measuring the change of something with respect to change in something else. If there is a change, you can calculate the non-zero slope that is associated with that change. Thus, it is quite simple to see the usefulness and the physical meaning of a derivative. This concept of differentiation, even though complicated, is readily understandable or relatable to our day-to-day events. Thus, calculus is everywhere, and it is essential for a thorough understanding of chemistry on a quantitative basis.

1.4.4 The second derivative and acceleration

Along these lines, we can construct the second and subsequent derivatives of functions. That is, the value of dy/dx itself can be a function of x and if we plot the slopes of the tangents at different values of x, as a function of x, we get a new function. If we draw tangents on this new function at any specific point, we get the value of the second derivative of the original function. While speed is the first derivative of distance traveled with respect to time, acceleration is the second derivative of the distance traveled with respect to time. It would be useful to plot dy/dx of the black line in Figure 1.2, as a function of x and obtain the second derivative at any specific x-value. Thus, the second derivative is also of physical significance, and we encounter this in our daily life.

Furthermore, we can have a derivative of a derivative of a derivative, which is the third derivative of the original function, etc., These are to be distinguished. You have already studied this kind of derivatives of functions in your math courses, and if in doubt, consult your mathematics books on these topics.

1.4.4 Partial derivatives and their physical significance

Along the above line of thought, we need to know partial derivatives because we will often have functions containing more than one variable, not just two, and we are interested in quantifying the change or changes that are occurring in our system. It will be important to review your knowledge of partial differentiation and consult your notes. Briefly, say that you have a function consisting of three variables, x, y, and z and you would like to write a partial derivative of one of the three variables with respect to a second one while keeping the third variable constant (equation given below).

$$dy = \left(\frac{dy}{dx}\right)_z dx + \left(\frac{dy}{dz}\right)_x dz$$

Value of dy will have two contributions, one coming from the infinitesimal change in x and another with respect to that of z. The net change in y will be the sum of changes induced by x as well as by changes induced by z. We write the exact differential dy as the sum of two terms, as above, where each term accounts for a change in y due to changes in either x or z, while the third is being kept constant, and the sum gives us the net change in y due to changes in x and z.

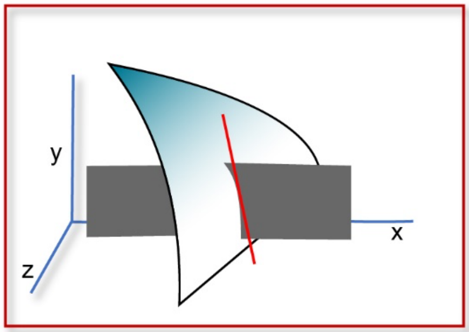

Figure 1.3 Partial differentiation and tangent on a 3-dimensional surface.

In terms of graphical interpretation of partial differentiation, consult Figure 1.3. The function relating the three variables is a three-dimensional surface such as the one in the above figure. This function is a surface because we have three distinct variables to plot. The values of points on the surface of this plot are drawn in such a way that the surface is not bending along the z-axis (this is not necessary), and it is coming out of the screen and bending towards the y-axis. This can be considered as a small part of the surface of a larger domain, for example. By extrapolation of this scenario, if you have more than three variables in a function, we get a more complex function that will be hard to visualize but the corresponding derivatives can be obtained by differentiation of the function with respect to the variable of interest while keeping all other variables constant.

What does this mean to us and how do we visualize the surface and its tangents? Well, consider the black rectangle drawn parallel to the x- and y-axes, cutting the z-axis at some fixed value (Figure 1.3) but perpendicular to the z-axis. This immediately means that the rectangle provides a curve where it cuts the surface of interest, and this curve along the surface has a fixed z-value but it is a function of only x and y. Thus, we can reduce the three-variable function into a two-variable function by holding z at a constant value.

Any tangent drawn on this curve gives the rate of change of y with respect to x but at a constant z-value. This is the first term in our partial derivative of y shown above, and the change in y due to change in x is equal to dy/dx at a constant value of z. When we multiply this derivative with dx, then we get a net change in y due to a change in x at constant z. We multiply by dx because dy/dx is the rate of change or change in y per unit change in x (miles per gallon that we discussed above), and only when we multiply the derivative with dx, we get the net change in y due to change in x, but of course at constant z.

Now, we write the change in y due to changes in z, in a similar fashion except that the rectangle will be drawn parallel to the z-axis but perpendicular to the x-axis at a constant x value. Then, the change in y due to change in z is given by dy/dz at constant x multiplied by dz, as we did before. This is the second term in the above equation, and it provides the net change in y as we change z while keeping x constant. Therefore, the sum of the above two terms, change in y due to x alone plus the change in y due to z alone, gives the total change in y due to changes in x and y, and this expression is valid for all exact differentials.

1.5 Integration and its Physical Significance

A brief discussion of integration is necessary for our discussions, but this section is not intended to supplement what you learned in your math courses. Integration of say $\frac{1}{x}$dx or functions like xdx, x^2dx or integration of trigonometric functions is very important for our discussion. We need to know how to integrate within given limits or integrate with an integration constant. You are strongly urged to consult the extensive tables of integrals for problem solving and derivations.

What does an integral mean? In graphical terms, the integral of a function is essentially the area under the curve within the defined limits. These are the upper and lower limits of the integral (Figure 1.4). Limits are chosen to suit our needs to solve the problem at hand.

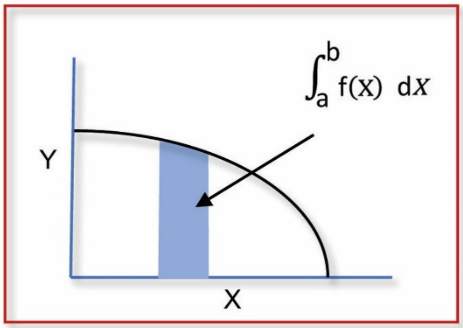

Figure 1.4 Integral of a function (black curve) is the area under the curve within the two limits, vertical lines drawn perpendicular to the X-axis.

In very simple terms, integration gives us the area under the function bounded by the lower and upper limits of the integral, while differentiation gives us the slope of the tangent drawn at a specific point on the function. We can integrate only continuous functions, and this can be done graphically by constructing small rectangles of width dx at every y-value while moving along the x-axis by infinitesimal increments of x. The sum of the areas of all such rectangles between the two limits is the integral of the function within those limits.

Example 1.6

Gallons of gas consumed during a trip is the integration of the function gallons per mile consumed by the car as a function of the distance we drive. The area under this curve from the beginning (lower limit) to the destination (upper limit) gives the total gas consumed during the trip, this is displayed by the gasometer. Alternatively, one can measure the volume of gas before and after the trip and estimate the gas consumed but that will not illustrate the process of integration.

We typically use differentiation followed by integration as an elegant mathematical trick to generate new functions and you will see those details as we advance in this book. The above mathematical descriptions of functions and operations are to be kept in mind to gain a physical basis for equations of physical chemistry to gain a deeper understanding of the changes that may be taking place in our system.

1.6 Applications in daily life

Several examples of mathematical functions and operations are given in the above discussions. More examples are given here.

1.6.1 Applications of linear equations

At the grocery store, let us say, tomatoes are being sold at 1$/lb and you need 5 lb. How much do you expect to pay? This is a linear equation (y = mx+c) where cost = price per lb x number of pounds = 1$x5 = 5$. In this example, let us recognize that price per lb is the first derivative, the slope of the line, and the intercept is zero, as zero tomatoes cost 0$.

My brother taught me how to calculate the price of 20 pencils when the cost of 5 pencils (P$) is given. He said to calculate the price of one item first, and that is P$/5, which is also the first derivative of price with respect to the number of items. Thus, he taught me differentiation at an early age. Then, he asked me to multiply the price per item with the number of pencils to be bought, and we get the total cost = (P$/5)x20 or y = mx+c, where m = P$/5, and c=0. This is a linear equation where the slope is the price per pencil and zero intercept (c). The intercept is 0 because 0 pencils cost 0$.

1.6.2 Applications of exponential functions

Most natural processes are exponential functions. If we puncture a plastic cup of coffee at the bottom, the coffee will drain out such that the height of the coffee column in the cup decreases exponentially. That is, coffee drains out quickly in the beginning and slows down as it's heigh reaches the bottom. At the beginning of the pandemic, the number of positive infections grew exponentially since each infected person could infect many others. Then, the rates flattened out as more and more people began practicing personal hygiene and social distancing.

1.6.3 Applications of the trigonometric functions

There was a big tree in my backyard leaning to one side. As time progressed, the lean increased, naturally. If mg is the weight of the tree above ground, what is the force acting on the tree to increase the lean? Trigonometry tells us that the force is 1-Cos(ø), where ø is the lean angle with respect to the vertical. When ø=0, there is no force to topple the tree and as ø increases, the force on the tree also increases as 1-Cos(ø). So, the tree had to be cut down when ø became too large for the tree to be stable.

Taking ø as the angle between the small needle and the large needle of the clock on the wall, when will the value of Sin(ø) be zero again, right after midnight? At roughly 1:05 am, after midnight the two needles nearly overlap giving our function a value of zero. If we plot this function for a 12 h period, we generate a periodic function, identical to the one shown in Figure 1.1C.

Example 1.7

As the sun rises in the east and travels across the sky, the intensity of light reaching the surface is Sin(ø) where ø is the angle sunrays make with the horizon. Thus, maximum intensity is at high noon, when ø=90˚, and approaches zero at sunset or sunrise. Thus, this trigonometric function played a very important role in planning our day and the construction of the concept of time.

1.6.4 Calculus in daily life

We already looked at the operations of differentiation and integration, and some examples and these are in our daily experiences. Price per item, miles per gallon, or miles per hour are first derivatives. While velocity is the first derivative, acceleration is the second derivative. Similarly, price per item interest rates, etc., are also first derivatives. When the interest rate is compounded daily, it is calculated per 100$ per day, or it is a function of both the principal as well as the number of days the loan was taken.

Example 1.8

Integration is also used commonly, sometimes without our knowledge. Let us consider that the utility company charges for the total amount of power consumed by you in a month. If the company monitors the power consumed each second throughout the month (infinitesimal change), then integration of the plot of power consumed per day vs seconds from the beginning of the month till the end, gives the total power consumed. Presumably, the power meter set up by the utility company does exactly this. Similarly, the consumption of water or gas at your house is monitored as a function of time and integrated by the water meter to give total consumption per month.

1.7 Key points

1. Mathematics plays a very important role both in physical chemistry as well as in daily life, and we recognized some of these examples.
2. We recognized linear functions, exponential functions, trigonometric functions, and others
3. The concepts of calculus have been related to operations in physical chemistry as well as daily life examples.

1.8 New terms and units

We recognized new terms such as specific functions, differentiation, and integration.

1.9 Self Reflection

Based on the material presented in this chapter, attempt to address the following:

1. Consider the space of your dorm room, and list properties in that space that follow linear, exponential, or trigonometric functions.
2. In the space of your car, list examples of first and second derivative properties you discover there.
3. Give examples of integration and differentiation, as experienced in our daily lives.
4. How do you determine the maxima and minima of a function?
5. What should be the value of the second derivative at the maximum value of a function?
6. Express an exponential function in terms of trigonometric functions.
7. What is the chain rule?
8. What is the value of e^x when x=0?
9. Within the space of your home, give three examples of a growing exponential functions.
10. As you drive to the university, cite 3 examples of first derivative functions that you might encounter.

1.10 Further Reading

1. Physical Chemistry 2nd Edition by K. J. Laidler, and J. H. Meiser, 'Appendix C: Some Mathematical Relationships', Houghton Mifflin Co., Boston (1995).
2. https://ocw.mit.edu/high-school/mathematics/
3. http://www.ocw.titech.ac.jp/index.php?module=General&action=T0300&GakubuCD=1&GakkaCD=311300&KeiCD=13&KougiCD=201601741&Nendo=2016&lang=EN&vid=03

1.11 Self Tests

1. A cubic function is
   a. $y = a x^2$
   b. y = ax
   c. $y = ax^3$
   d. y = 1+ x
   e. none of the above
2. An example of a trigonometric function is
   a. y = ax
   b. $y = ax^2$
   c. y = Cos(x)
   d. y = ln (x)
   e. none of the above
3. An example of a first differential of a function is
   a. 55 miles per gallon
   b. 55 miles
   c. 55 gallons
   d. area
   e. none of the above
4. The integral of the function, $dy = x^3\,dx$ from x = 2 to x = 6 is
   a. 12
   b. 320
   c. 324
   d. 4

5. The integral of 1/x dx is
    a. x + c
    b. ln(x) + c
    c. x^{-2} + c
    d. 1/x +c
6. The second derivative of y = cos(x) with respect to x is
    a. sin(x)
    b. –sin(x)
    c. cos(x)
    d. –cos(x)
7. The exact differential of a state function is
    a. $\mathrm{dy} = \left(\frac{\mathrm{dy}}{\mathrm{dx}}\right)_z \mathrm{dx} + \left(\frac{\mathrm{dy}}{\mathrm{dz}}\right)_x \mathrm{dz}$
    b. $\mathrm{dx} = \left(\frac{\mathrm{dy}}{\mathrm{dx}}\right)_z \mathrm{dx} + \left(\frac{\mathrm{dy}}{\mathrm{dz}}\right)_x \mathrm{dz}$
    c. $\mathrm{dy} = \left(\frac{\mathrm{dy}}{\mathrm{dx}}\right)_z \mathrm{dy} + \left(\frac{\mathrm{dy}}{\mathrm{dz}}\right)_x \mathrm{dz}$
    d. $\mathrm{dy} = \left(\frac{\mathrm{dy}}{\mathrm{dx}}\right)_z \mathrm{dx} + \left(\frac{\mathrm{dy}}{\mathrm{dz}}\right)_x \mathrm{dx}$
    e. none of these
8. What is the integral of y = x^2 dx?
    a. 2x + c
    b. $1/2x^3$ + c
    c. $1/3x^3$ + c
    d. 2x
9. What is the derivative of y = ln (x)?
    a. 1/x
    b. 1
    c. log (x)
    d. x
    e. none of the above
10. Integration is equivalent to
    a. area under the curve
    b. logarithm of a function
    c. differential of a function
    d. partial derivative of a function
    e. none of the above
11. Differentiation is equivalent to
    a. the rate of change of a function
    b. Integral of a fraction
    c. Integration
    d. Partial derivatives
    e. none of the above
12. The second derivative is
    a. the rate of change of a function
    b. Integral of a fraction
    c. the first derivative of a first derivative
    d. Partial derivatives
    e. none of the above
13. First derivative of x^2 is
    a. 1/x
    b. 2x
    c. x/2
    d. 2
    e. none of the above
14. First derivative of cos (x) is
    a. 1/x

b. sin (x)
c. – sin (x)
d. 2
e. none of the above

15. Integral of (1/x) dx is
    a. 1/x
    b. sin (x)
    c. – sin (x)
    d. ln x+ constant
    e. none of the above
16. Integral of ($1/x^2$) dx is
    a. 1/x
    b. sin (x)
    c. – sin (x)
    d. ln x
    e. none of the above
17. Division of y by x will give a value greater than y, when
    a. x = 0
    b. $0<x<1$
    c. $x > 1$
    d. x = infinity
    e. none of the above
18. Value of 1/x when x approaches zero, is
    a. infinity
    b. - infinity
    c. 0
    d. 1
    e. none of these
19. Value of 0/2 is
    a. infinity
    b. - infinity
    c. 0
    d. 1
    e. none of these
20. The second derivative of e^x is
    a. infinity
    b. e^{2x}
    c. e^x
    d. 1
    e. none of these

1.12 Self Tests Key

1.c, 2.c, 3.a, 4.b, 5.b, 6.D, 7.a, 8.c, 9.a, 10.a, 11. a, 12. c, 13. b, 14. c, 15.d, 16. e, 17. b, 18. A, 19. c, 20. c.

1.13 Problems

1. Integrate the function $dy = x^3\,dx$ within the limits of $x = 2$ to $x = 6$ (Ans. 320)
2. What is the graphical equivalence of integration? (Ans. Area under the curve)
3. At what value, division of y by x will give a value greater than y? (Ans. $0<x<1$)
4. What is the second derivative of e^x with respect to x? (Ans. e^x)
5. What is the slope of the tangent drawn to a function at a given point equals to? (Ans. first derivative)
6. Expand the exponential function into a power series.
7. What is the approximate value of e^x when x is very small?
8. Write the exact differential of $f(x,y,z)$.
9. Write the partial differential of $f(x,y)$ with respect to x, at constant y, and with respect to y, at constant x.
10. Integrate $f(x) = ax^2\,e^x\,dx$ with the limits $x = 0$ to 10, where a is constant.

Chapter 2. The Kinetic Theory of Gases

After completing this chapter, you will be able to:

- Synthesize the ideal gas equation from the kinetic theory of gases using the Newtonian mechanics
- Relate the bulk properties of gases such as pressure, volume, temperature, and mole numbers with its microscopic properties such as mass, velocity and molecular mass.
- Develop mathematical equations for the average squared velocity ($<c^2>$) and root mean square velocity of the gas particles.
- Begin an inquiry into the atomic or molecular nature of the gas and examine the molecular descriptions of gas pressure.
- Deduce the internal energy and total kinetic energy of the ideal gas.

Goals

- Develop the kinetic theory of gases and connect bulk properties of the gas such as pressure, volume, mass, molecular speed, and number of particles with the atomic/molecular properties such as particle mass, number of particles, and their velocity.
- Use Newtonian mechanics in the development of the kinetic theory of gases.
- Discuss microscopic descriptions of the macroscopic properties of the ideal gas.
- Construct expressions for gas pressure, kinetic energy, average velocity, and root mean square velocities of the ideal gas
- Discuss salient features of the equations and their relevance to day-to-day experiences.

2.1 Why study this?

Gases are, by far, the simplest of substances to investigate. Even though the gas particles are not visible to the naked eye, we can readily feel their presence around us, and we are constantly influenced by their physical and chemical properties. Precise understanding of gas behavior is central to weather forecasting which depends on our ability to accurately model gas properties under specific conditions of temperature, pressure, gas velocity, humidity, and altitude. Gases are also used in a variety of chemical applications where modeling of their properties is critical for scientific instrument design, power production, or process control. The study of the various chemical phenomenon is readily possible with gases and gases to form a firm basis to develop a detailed understanding of large-scale chemical reactions. For example, the internal combustion engine operates by the reaction of oxygen with gasoline vapor, while modern fuel cells often use gaseous hydrogen or methane and oxygen as reactants to produce electrical energy. Most combustion processes use gaseous oxygen as the oxidant. In our environment, the ozone layer in the upper atmosphere is essential to screen harmful UV radiation from reaching the surface of the planet. Gases are also important for biological systems, providing necessary reactants for energy output or as byproducts of metabolic processes. Most of our oxygen on this planet, for example, has been generated by biological processes. In contrast, oxygen consumption is essential to most biological systems. We can't live for more than a few minutes, for example, without air and covid patients often needed large quantities of medical oxygen.

Our primary goal in this chapter is to relate bulk macroscopic properties of gases with their microscopic atomic or molecular properties. This kind of correlation of molecular or macroscopic properties with bulk properties helps in the molecular design of new matter with novel properties, which is one of the major applications of the discipline of Chemistry, the central science.

2.2 The kinetic theory of gases

The model of the Kinetic Theory of Gases was proposed by Clausius in 1857[5] but it was not accepted by the community until the analysis of Brownian motion by Einstein in 1905[6] which supported the basic descriptions of kinetic theory. Several simplifying assumptions were made in this theory which was followed by simple mathematical steps to arrive at the gas equation for pressure. The gas equation was then able to explain a large body of experimental data at the molecular level. This theory expanded our view of the matter at the molecular level and introduced the new dawn of atomic/molecular chemistry. This theory was later updated multiple times to include more modern descriptions of matter.[7]

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[5] Clausius, R., Ueber die Art der Bewegung, welche wir Wärme nennen", *Annalen der Physik*, **1857**, *176* (3), 353–379.

[6] Einstein, A., Über die von der molekularkinetischen Theorie der Wärme geforderte Bewegung von in ruhenden Flüssigkeiten suspendierten Teilchen" (PDF), *Annalen der Physik*, ∫**1905,** *17* (8), 549–560.

Here, we introduce specific assumptions of the kinetic theory of gases, listed below, and then build a mathematical model describing the gas properties and rationalize relationships between different properties of gases.

2.2.1 Assumptions of the kinetic theory of gases

All gases consist of a very large number of very small particles.

Here, a large number means numbers on the order of 10^{20}, $10^{25,}$ etc. on the order of Avogadro's number, ~6.203×10^{23} per mol. Therefore, we assume that ordinary gas samples in the laboratory, under normal conditions will have an excessively large number of molecules or atoms (particles).

Particles of very small volume mean that these particles are so small that the net volume of the particles themselves is much less than the container volume (V). If N is the number of particles, V_i is the volume of the i-th particle, then the sum of the volumes of all the N particles ($\sum V_i$) is <<< gas volume (V) or $\sum V_i = 0$. This is an important assumption.

In real gases, however, the molecular volumes are not negligible. That is when we cool a real gas it liquefies and then solidifies, eventually. Thus, the volume of particles of a real gas is finite, comparable to that of its solid form, but we will assume that particle volume is negligible. If you want to make precise measurements, we need to take into account the finite volume of gas particles in real gases, which we will examine in a later chapter. For now, we will assume that particles are so small that $\sum V_i = 0$.

The particles do not attract or repel each other.

We assume that the interparticle interactions are too weak and set to zero. As described above, a real gas can be condensed into a liquid and then to a solid which implies that there are interparticle interactions that are not negligible. Careful introduction of these interactions can refine our model, but it also adds mathematical complexity. This task is deferred to a later chapter. We assume that each particle does not experience any force of attraction or repulsion from any other particle in the gas sample.

The particles are in constant motion, collide with each other and with the container wall, but never come to rest because the collisions are perfectly elastic.

The particles keep moving and moving. When they are moving, they move in straight lines because no force is acting on them (non-interacting), until they collide with each other or with the wall. So, we can apply Newton's laws of motion to calculate their momentum and direction of motion. Only when they collide, they're likely to change their direction. These collisions with each other and with the container are perfectly elastic or else they will come to rest and condense spontaneously. This does not happen. Thus, we assume that the collisions are perfectly elastic, and the gas particles never come to rest by themselves. This was proposed by Bernoulli in 1738 but was not accepted until much later.

The pressure exerted by the gas is due to the total force the gas particles exert on the container wall due to their constant collisions with the wall.

The total force exerted by the gas particles due to their collisions on the container walls is translated to pressure because force per unit area is pressure. Thus, the constant bombardment of the vessel walls by the particles is responsible for the gas pressure. We will use this mechanical insight in deriving an expression for gas pressure by the kinetic theory of gases. The following description at the molecular level is useful to follow the derivation.

Imagine a gas container with blue dots and arrows depicting the direction that they are moving (Figure 2.1A). Note how arrows are pointing in various directions, randomly. So, the gas particles are randomly moving within this container, indicated by the arrows. Let m be the mass of each particle. We will assume that our gas container is a rectangular box and aligned with X, Y, and Z-axes and that the particles bounce off the wall due to the perfectly elastic collisions with it (Figure 2.1B). This scenario is convenient for our derivation but later we will show that this scenario is not essential and does not impact the equation derived.

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[7] R. L. Liboff (2003). *Kinetic Theory: Classical, Quantum, and Relativistic Descriptions*, third edition (Springer).

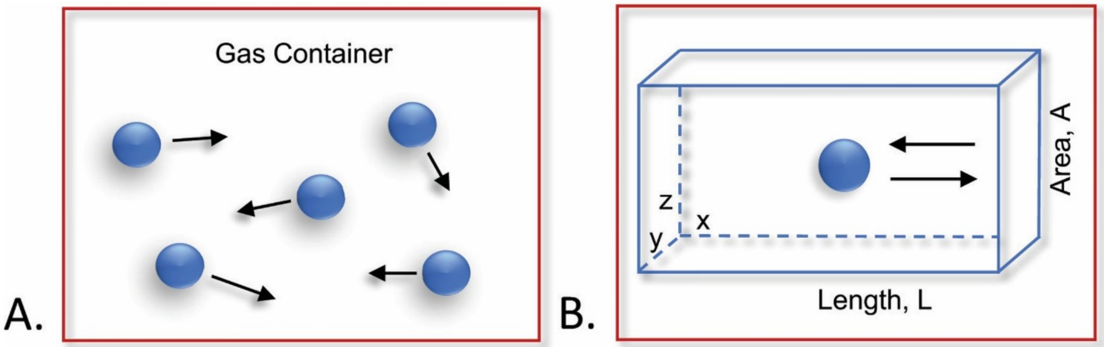

Figure 2.1 A. Gas particles (blue dots, not drawn to scale) moving in random directions (arrows) in a container. The particles are too small to be visible to the naked eye, have finite mass but negligible volume. The particles are in constant random motion colliding with each other and with the container. B. Collisions with the container and with each other are perfectly elastic and thus, the particles never come to rest.

Now, we assume that the gas container of length L has a rectangular cross-section of area A and our particle in question is moving with velocity u_i, parallel to the X-axis (Figure 2.1B). This is an important assumption, and we will elaborate on this later and see what changes we need to make for a random motion of our particle with an arbitrary velocity. We will also question the assumption that our container is a rectangular box and how we will accommodate any shape for the container. But it is important to neglect these issues at this stage.

Our particle is somewhere in the box, and it is moving along the X-axis. The particle need not be at the beginning, center, or end of the box. It is randomly chosen to be somewhere in the box.

2.3 The pressure equation

Our strategy for arriving at an expression for pressure is as follows. We will use classical mechanics, and calculate the force exerted by one particle on the walls of the gas container by using Newton's laws of motion. Then, we will calculate the force exerted by one particle per unit area of the container wall, or the pressure due to one particle. Next, we will calculate the pressure exerted by all particles that are moving in random directions.

2.3.1 Pressure exerted by one particle

We will first compute force as the rate of change of momentum when one particle hits the wall. Then, we will calculate the number of collisions made by this one particle in one second as it bounces back and forth in the box. This back-and-forth motion will continue forever because collisions are perfectly elastic. Our particle is moving perpendicular to the right and left walls, which are placed perpendicular to the X-axis. We will use the following steps to get pressure due to one particle.

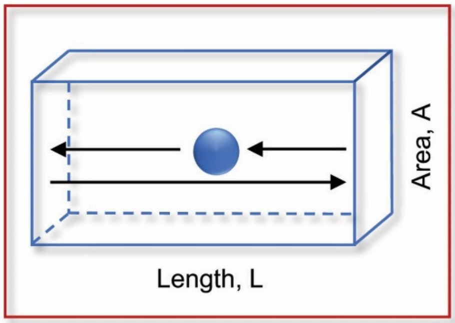

Figure 2.2 Gas particle (blue dot, not drawn to scale) moving along the X-axis hits the right wall which is placed perpendicular to the X-axis. Then it bounces back, collides with the left wall, and travels a round trip distance of 2L before colliding again on the right wall. Thus, it travels a distance of 2L between successive collisions, regardless of where we choose to place the particle in the box.

1. The initial momentum of the particle when it is about to hit the wall is mu_i and the final momentum after it bounces back is – mu_i. So, the change in momentum due to one collision is ($-mu_i - mu_i$) = $-2mu_i$.
2. The particle collides with the wall on the right side, each time it completes one round trip, or a distance of 2L, and hence, the number of collisions it makes with the right wall, in one second = $u_i/2L$. This is because the particle is traveling u_i meters in one second and hence, it makes $u_i/2L$ round trips in one second.
3. The rate of change in momentum of the particle is the number of collisions in one second multiplied by the change in momentum in one collision. That is given as, $(-2mu_i)(u_i/2L)$ or $-2mu_i^2/2L$ or $-m\,u_i^2/L$.
4. The force exerted on the particle by the wall is the rate of change of momentum or change in momentum of the particle in one second, or $-m\,u_i^2/L$.
5. We are interested in the force exerted by the particle on the wall but not the force exerted by the wall. Because the collisions are perfectly elastic, the force exerted on the particle is equal and opposite to the force exerted on the wall. Thus, the force exerted by the particle on the wall is $-(-m\,u_i^2/L)$ or $m\,u_i^2/L$.
6. The pressure exerted by one particle is force per unit area, and hence pressure due to one particle is $m\,u_i^2/LA$ or $m\,u_i^2/V$ where volume V = L A.

2.3.2 Pressure exerted by all the particles combined

The pressure exerted by N particles in the container will then be equal to the sum of the pressures exerted by all the N particles. Since each particle may be traveling at a different velocity, we need to sum up the pressure exerted by each particle. This is total pressure (p), which is readily obtained as

$$p = \sum m\,u_i^2/ V$$

where i varies from 1 to N, and the velocity of each particle is explicitly included, m is constant for a pure gas sample. However, we do not know the velocities of individual particles, but we can express them in terms of the average velocity squared along the X-axis as,

$$<u^2> =(u_1^2 + u_2^2 + u_3^2 + u_4^2 .....)/N \qquad \text{or}$$

$$\Sigma u_i^2 = <u^2> N$$

Here, we summed all the individual velocities after squaring them, so that positive and negative velocities do not cancel, and then divided by N to obtain the average velocity. We now replace Σu_i^2 by the average squared velocity $<u^2>N$ to get the total pressure of the gas as,

$$p = m\,N <u^2>/V$$

We also note that the average squared velocity of the particles in any direction $<c^2>$ can be written in terms of the velocity vectors along the X-, Y- and Z-axis as,

$$<c^2> = <u^2> + <v^2> + <w^2>$$

where u, v, and w are the velocity vectors along the three Cartesian coordinates, X-, Y- and Z-axis, respectively.

We also recognize that the average squared values of each of these vectors must have the same value, because the gas is stationary in the container and not flowing, and on an average, it is not flowing in any given direction. Hence,

$$<u^2> = <v^2> = <w^2>$$

$$<c^2> = 3 <u^2> = 3 <v^2> = 3 <w^2>$$

$$<u^2> = 1/3 <c^2>$$

By substituting this value in the previous equation for pressure, we get,

$$p = (1/3)\ \mathrm{N\ m} <c^2>/\mathrm{V}$$

Or we can rearrange it as:

$$pV = (1/3)\ \mathrm{N\ m} <c^2>$$

This latter equation resembles the ideal gas law where the right side is to be equal to nRT.

Example 2.1

Calculate the pressure of an ideal gas of volume 22.4 L, consisting of 1 mol of particles, the molecular mass of 4 g/mol, and the RMS speed of 1400 m/s.

Start with pV = (1/3) N m $<c^2>$. We have V, $\sqrt{<c^2>}$ and molar mass, m = molar mass/Avogadro number.

Convert the molar mass into molecular mass by dividing it with the Avogadro's number

$$p = \left(\frac{1}{3V} N\ m < c\hat{}2 >\right) = \frac{1}{3}\ \frac{1000\ L}{22.4\ L\ m\ m\ m} N\ \frac{0.004\ kg}{N}\ \frac{1400\ m}{s}\frac{1400\ m}{s} = 116666\ \frac{kg}{m\ s\ s} = 116.7\ kPa$$

The quantity, pressure, has several different units, and their use is justified in different contexts of daily activities in both academia and industry. Thus, we need to be familiarized as to how to interconvert these units, which are summarized in Table 2.1. The technical atmosphere (at or kg-f) is 1 kg/cm^2, Barad is 1 dyne/cm^2 and Pieze (pz) is a pressure unit used in the Soviet Union and 18th century France.

Table 2.1 Units of pressure

Atm	*kPa*	*Torr*	*bar*	*psi*	*Torr*	*mmHg*	*Kgf/cm^2(at)*	*Pieze (pz)*	*Barad (Ba)*
1.0	101.325	760	1.013	14.69	760	760	1.033	0.1	1,013,250

2.3.3 Physical descriptions of the pV equation

This is derived from fundamental principles by applying Newtonian mechanics. We will look at the pressure of the gas in slightly more detail, examine how macroscopic quantities are related to the microscopic quantities. We recognize that 1/3 is a constant, N is the number of particles, m is the mass of each particle, and $<c^2>$ is the average squared velocity in any direction or speed.

First, we would say that pressure of the gas is related directly to the number of particles in the container. So, if we increase the number of particles in the container, we'll increase the pressure. This is very evident on a day-to-day basis. For example, as you pump more air particles into the bicycle tire, the tire having a fixed volume, the pressure increases. Thus, the pressure is proportional to the number of particles.

Pressure also depends on the mass of the particles. Heavier particles exert higher pressure according to the equation pV= 1/3 N m $<c^2>$, as m is the mass of the gas particle.

For one mole of a substance, N m is the molecular weight of the gas. So, the average speed, $<c^2>$ can be obtained if we measure the pressure and volume of one mole of a gas at a given temperature. In the above derivation, we implicitly assumed that the gas temperature is constant, but this equation is a wonderful way to try to understand the macroscopic properties such as average squared speed.

Last but not the least, pressure is inversely related to volume, V, when all other values are constant and this is proved to be the case by Boyle's law, which we will examine in the next chapter.

One other point to consider is the pV term and its units. Pressure times volume has the units of energy (joules), and therefore, 1/3 N m $<c^2>$ is the pV energy of the gas. Because we assumed that there are no inter-particle interactions, the gas has no potential energy, and all its energy is kinetic energy. Then, multiplying both sides of the above equation by 3/2, we get (3/2) pV = (1/2) Nm $<c^2>$ or total kinetic energy of the gas is given as (3/2) pV or pV energy is less than the total energy of the gas. Thus, the kinetic energy of the gas is greater than the pressure-volume energy, a new insight into the nature of energy and matter. We will discuss more on pV energy when we discuss enthalpy. We found a simple way to relate pV energy to the kinetic energy of the gas. We will get back to this equation in the next chapter and relate the kinetic energy with the temperature of the gas.

2.3.4 Validity of the assumptions

We assumed that the particle is moving along the X-axis. But the particles are moving randomly, not all of them are moving along the X-axis. Any particle moving in any given direction can have velocity components along the X-, Y- and Z-axes (u, v, and w, the velocity vectors). Thus, we can decompose the velocity vector of any particle in any direction in terms of the velocity vectors along the three axes. And this is exactly what we have done. We have related the velocity along the X-component with the vector in a random direction. Thus, we accounted for the random motion of the particles in any given direction.

We assumed a rectangular box for the derivation. Since the pressure exerted by the gas is independent of the shape of the container, that is, pressure is isotropic and equally exerted on all walls of the container, the shape of the container is of no consequence. Thus, a rectangular box, chosen for convenience, does not affect the above derivation.

We also assumed that the particles are elastic making elastic collisions with the wall with each other. If this breaks down, then there will be a loss in the kinetic energy of the particles and at some point, the particles will come to rest. That is, if this is true then the gas should spontaneously condense into a liquid at any temperature and pressure. But we don't see gases condensing spontaneously into liquids or solids, and therefore, this is a valid assumption.

We also assumed that the volume of the particle is negligible and that inter-particle interactions are negligible. We will examine these two assumptions in detail when we discuss the van der Waals equation in a later chapter. So, except for these two assumptions, all the rest seem to be good so far.

We note that we did not arrive at the ideal gas law, which was proposed by Clapeyron in 1834 based on Boyle's Law, Charles' law, and Avogadro's hypothesis, and we will discuss this in the next chapter. In addition to the above gas properties, the kinetic theory of gases also explains several other properties such as temperature, diffusion, thermal conductivity, viscosity, and other properties of gases which we will be learning in later chapters. For a chart describing the central role of the kinetic theory with other thermodynamic concepts see this external link.[8]

2.4 Molecular speeds and the root mean squared velocity

Now, we ask how fast a molecule travels from point A to B, or we can ignore the direction and ask the question, what is the speed of my molecule? We can amazingly deduce these sorts of properties of molecules from the pV equation,

$$\mathrm{pV} = 1/3\ \mathrm{N\,m} <\mathrm{c}^2>$$

As we squared the velocity, the directional information is lost, and the value of average squared speed is the same as average squared velocity. The brackets indicate that we're talking about the average value. So, we can readily calculate the value of $<c^2>$ under specific conditions without a direct measurement of the speed. When n= 1 mol, N is Avogadro's number and since m is the mass of one molecule, Nm = M, the molar mass of the gas. By substituting these values in the above equation, we get the expression for the average squared speed, or by taking the square root, we get the root mean square (RMS) speed of the gas molecule in terms of pressure, volume, and molar mass or RT.

$$\sqrt{}(3\mathrm{pV/M}) = \sqrt{<\mathrm{c}^2>} = \mathrm{RMS\ speed} = \sqrt{\frac{3RT}{M}}$$

We recognize three interesting situations.

1. The RMS speed of the gas particle increases as the pressure of the gas increases at constant V, when we simply heat the sample, keeping the number of moles constant. Thus, the particles move faster and faster with an increase in temperature and this increase in speed increases the pressure

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[8] http://hyperphysics.phy-astr.gsu.edu/hbase/Kinetic/ktcon.html

exerted by the gas via an increased number of more energetic collisions with the wall. We will recall this result again when we discuss Charles' law in the next chapter.

2. The RMS speed is inversely proportional to the square root of molar mass, at constant pressure, mole numbers, and volume. A small molecule such as H_2 will be zipping around much faster than the slightly heavier molecule such as oxygen, and much faster than a protein of say, M = 50000 Daltons.
3. If molecular collisions are important for a chemical reaction, then lighter molecules will react faster than heavier ones, as they move faster and collide more often. This formed a basis to separate heavier deuterium isotope from the lighter protium.

Example 2.2

One mole of helium gas at 1 atm pressure and 273.15 K, calculate $\sqrt{<c^2>}$.

We have p = 1 atm, V = 22.4 liters, M= 0.004 kg/mol

$$\sqrt{< c^2 >} = \sqrt{[\frac{3RT}{M}]} = \sqrt{\frac{3x\ 8.314\ (kg/mol)(m\ m/s\ s\ K)\ x\ 273.15\ K}{0.004\ \ kg/mol}} = \sqrt{\frac{3\ x\ 8.314\ x273.15}{0.004}\frac{m\ m}{s\ s}} \sim 1305 \text{ m/s}$$

2.5 Average kinetic energy and average total energy of gas particles

Now, we will ask the question how much energy does my molecule carry, as it is zipping around in the gas? Because the ideal gas has no inter-particle interactions, all its energy is kinetic, and it has essentially no potential energy. We can calculate the kinetic energy (KE) of the particle because we know its average velocity. So, from Newtonian mechanics, the average KE of the molecule (ε, Epsilon) is simply equal to (1/2)m$<c^2>$. The total KE of the gas is obtained by multiplying this value with the total number of particles in the gas, N.

$$<\varepsilon> = (1/2)\ \mathrm{m} <C^2>$$

$$\mathrm{N}<\varepsilon> = (1/2)\ \mathrm{Nm} <C^2>$$

The total energy of the gas sample is defined as the intrinsic energy of the system and is given the symbol U, the internal energy of the gas. Since all its energy is purely kinetic due to lack of interactions between gas particles, we can simply obtain the U of the gas in terms of its pressure and volume, as

$$\mathrm{U} = (1/2)\ \mathrm{Nm} <C^2> = (3/2)\ \mathrm{pV} \quad \text{because } \mathrm{Nm} <c^2> = 3\ \mathrm{pV}$$

$$\mathrm{U} = (3/2)\ \mathrm{nRT}, \text{ using ideal gas law}$$

Thus, using the kinetic theory, we can calculate the internal energy of the gas, another major success of this model. This energy can never be less than 0, as average speed can never be <0.

Example 2.3

Calculate average energy of one mole of helium gas (U) at 1 atm (V = 22.4 liters).

$$\mathrm{U} = (3/2)\ \mathrm{p\ V} = \frac{3\ atm\ 22.4\ L}{2}\frac{J}{m\ m\ m\ atm}\ \frac{m\ m\ m}{1000\ L} = 33.6\ \mathrm{J}$$

In addition to the kinetic energy, the gas possesses pV energy, additional energy by virtue of its existence. That is, energy expended in creating certain space and certain pressure. Then, total energy of the gas is the sum of the pV energy and kinetic energy and equals to pV + (3/2) nRT or (5/2) nRT, we call this the enthalpy (H) of the gas and define it in later chapters. This energy can never be <0.

Example 2.4

Calculate average enthalpy of one mole of helium gas (H) at 1 atm (V = 22.4 liters).

$$\mathrm{H} = (5/2)\ \mathrm{p\ V} = \frac{5\ atm\ 22.4\ L}{2}\frac{J}{m\ m\ m\ atm}\ \frac{m\ m\ m}{1000\ L} = 56.0\ \mathrm{J}$$

2.6 Molecular interpretation

The expression connecting the pressure with their molecular mass and average squared speed is a useful connection between the bulk properties of the gas and its macroscopic properties. Thus, our first glimpse into the microscopic world is provided by this example. We related bulk properties (p V) with macroscopic properties (m, N, M, and c) and estimated the average kinetic energy of the gas particles. This energy is termed as the internal energy of the gas, U.

The average molecular speed and average kinetic energy of the molecules are interesting characteristics of the gas at the molecular level. These microscopic properties of the gas can be estimated by measuring the macroscopic properties, and it is the grand success of the kinetic theory of gases. We will use these insights in later sections to correlate other bulk properties of gases with these molecular descriptors.

2.7 Applications in daily life

The collective force exerted by the gas particles is often felt by us when the wind blows, and the awesome force of these particles is readily illustrated when a hurricane lifts boats off the harbor and tosses them onto the land. Thus, even though the particles are too small to be visible, their presence and the force exerted by them cannot be ignored.

The expression for pressure is related to most of the applications where gases are involved. For example, it is the pressure of the air which we check, and it is the air pressure that keeps our tires inflated. It also asserts the atmospheric pressure, and allows the dissolution of oxygen in water, supporting aquatic life. Pressure is the invisible player in our complex weather on the planet and other planetary systems with the atmosphere. Numerous other applications of gas pressure may be recognized in our daily lives.

Expressions for average speed and average energy are not directly used in daily life but we can readily relate several daily experiences with these quantities. For example, the average speed of the gas particles is increased with increased wind speed, where the velocity component aligned with the wind direction is far greater than in other directions. This in turn exerts greater pressure in that direction. Thus, we can certainly feel the pressure exerted by the gas particles as we walk against the wind in a storm.

The average energy of the particles is proportionately increased with speed and transfer of this energy to a boat bobbing in the boatyard can lift it and throw it onto the land far from the boatyard. The power of the gas particles traveling at excess of 200 miles per hour has been recently encountered during one of the Atlantic hurricanes in 2017 that wiped out the electrical power to the entire island of Puerto Rico. Here, the energy of the particles is mostly due to their velocity in one direction at room temperature.

High pressure in a steam engine, internal combustion engine, jet engine, or rocket engine is used for propulsion, and this involves the increase in the RMS speed of the gas particles with an increase in pressure. These energetic gas particles provide their kinetic energy for propulsion.

2.8 Key points

1. The kinetic theory of gases is a solid foundation to examine gas behavior at the molecular level.
2. Gas pressure is proportional to the number of particles, particle mass as well as the averaged square of their velocity.
3. Heavier gases exert higher pressure because they have greater momentum to transfer when compared to that of a lighter gas, at the same RMS speed.
4. A larger number of particles exert greater pressure due to the increased number of particle collisions per unit area per second on the walls of the vessel.
5. The root mean square velocity of the gas particles is proportional to the square root of their pressure and volume and is also inversely related to the square root of the molar mass.
6. The total energy of an ideal gas is its kinetic energy which is related to the number of particles, their mass, and RMS speed.

2.9 New terms and units

Pressure (p), mass of a gas particle (m), number of particles (N), gas volume (V), area of cross-section (A) of the container, container length (L), mean squared velocity ($<c^2>$), velocity components u, v, and w along the 3-axes. pV energy, Root Mean Square Speed ($\sqrt{<c^2>}$), Kinetic energy of the gas particle (ε), Total KE of the gas (U).

Pressure can be expressed in many different units, among which atmosphere (atm) is common. The SI unit for pressure is the pascal or one Newton of force exerted on unit area (square meter). It is also often expressed in mm of Hg column (torr) where 760 mm Hg column equals one atmosphere. RMS speed has the units m/s, same as speed or velocity but it is a scalar quantity. The unit of kinetic energy is the same as energy, joules.

2.10 Self reflection

Based on the material discussed in this chapter, evaluate the following challenges.

1. The pV energy of the gas is less than its entire kinetic energy. Since it has no potential energy, where is the missing energy?
2. What correction would you make if we do not neglect molecular volumes and what final expression would you arrive at, with this correction?
3. What correction would you make to the pV equation derived in this chapter, if we include intermolecular interactions?
4. Imagine that the gas is flowing along the X-axis at 100 miles per hour in an infinitely long container. What would be the pressure exerted by the gas on a sensor placed in the path of the gas?
5. Derive an expression for electron gas, where each particle has one unit of electrostatic charge.

2.11 Further reading

1. https://ocw.mit.edu/courses/physics/8-333-statistical-mechanics-i-statistical-mechanics-of-particles-fall-2013/video-lectures/lecture-7-kinetic-theory-of-gases-part-1/
2. https://ocw.mit.edu/courses/chemistry/5-112-principles-of-chemical-science-fall-2005/video-lectures/lecture-13-kinetic-theory-behavior-of-gases/
3. https://ocw.mit.edu/courses/physics/8-333-statistical-mechanics-i-statistical-mechanics-of-particles-fall-2013/video-lectures/lecture-8-kinetic-theory-of-gases-part-2/

2.12 Self Tests

1. The root mean square (RMS) speed of gas molecules increases (at constant V, n and M) with

a. increase in √(pressure)

b. decrease in temperature.

c. increases with molar mass.

d. increases with √(temperature)

e. none of these

2. If a particle of mass ‘m’ is moving perpendicular to the wall with a velocity ‘v’ and hits the wall as a perfectly elastic collision, the change in momentum of the particle is

a. 2mv

b. -2mv

c. 0

d. mv

e. –mv

3. Pressure is

a. Force per unit area

b. Momentum per unit time

c. Mass per volume

d. Temperature per time

e. none of these

4. A mixture of ideal gases contains n_1 moles of component 1, n_2 moles of component 2, and occupies volume V, the pressure exerted by the mixture is

a. n_1n_2RT/V.

b. $(n_1+n_2)RT/V$

c. $(n_1-n_2)RT/V$

d. $n_1/(n_2(RT/V))$

5. If an ideal gas occupies 24.93553 liters of volume at 100 kPa and 300 K, what is the number of moles of gas?

a. 2.2 moles

b. 9.6 moles

c. 1.0 moles

d. 0.1 moles

6. If a gas has density ρ at pressure p, what is its average velocity C_{rms} in terms of density and pressure?

a. $\sqrt{(3\rho/p)}$

b. $\sqrt{(3\rho p)}$

c. $\sqrt{(2p/\rho)}$

d. $\sqrt{(3p/\rho)}$

7. What is the average time required for a perfume molecule (vapor) of M = 0.1 kg/mol to travel a distance of 5 m at room temperature (T = 300 K)?

a. 0.002 s

b. 0.02 s

c. 0.2 s

d. 2 s

e. 20 s

8. What is the SI unit for pressure?

a. bar

b. atmosphere

c. Pascal

d. Torr

9. The symbol “N” is commonly used (as well as in this textbook) to denote which of the following?

a. number of particles

b. number of moles

c. molecular weight

d. area of the cross-section

e. none of these

10. What is the mean squared velocity for one mole of helium gas at standard temperature and pressure?

a. $3.404 \times 10^{12}\ s^2/m^2$

b. $3.404 \times 10^{12}\ m^2/s^2$

c. 1.135×10^{12} m^2/s^2

d. 1.135×10^{12} s^2/m^2

11. One of the key assumptions of the kinetic theory of gases is

a. the particles attract or repel weakly

b. the particles are too small to attract others

c. the particles are slippery

d. the particles repel each other

e. none of the above

12. One of the key assumptions of the kinetic theory of gases is

a. the particles come to rest now and then, before moving again

b. the particles are in constant motion

c. the particles do not collide with each other

d. the particles move avoiding collisions

e. none of the above

13. One of the key assumptions of the kinetic theory of gases is that

a. the gas consists of very large number of very large particles

b. the gas consists of very small number of very small particles

c. the gas consists of very large number of very small particles

d. the gas consists of very small number of very large particles

14. One of the key assumptions of the kinetic theory of gases is

a. the particles undergo elastic collisions with the wall and assert pressure

b. the particles undergo inelastic collisions on the wall and assert pressure

c. the particles do not collide with the wall and assert pressure

d. the particles are repelled by the walls and assert pressure

e. none of the above

15. The pressure exerted by one particle of mass m and velocity v moving along the length of the wall of a quadrilateral vessel of volume V is

a. mv^2/ V

b. mv/ V

c. $2mv/ V^2$

d. 2 mV

e. none of these

16. The pressure exerted by N particles of mass m and average velocity <c> moving randomly in a vessel of volume V is given as

a. (1/3)nm<c>

b. $(1/3)nm<c^2>$

c. (1/3)Nm<c>

d. $(1/3)nm<c^2>$

e. none of these

17. The total kinetic energy of the particle is the following thermodynamic quantity of the gas:

a. enthalpy

b. Gibbs free energy

c. internal energy

d. entropy

e. none of these

18. The RMS speed of gas particles of molar mass M at pressure p, occupying volume V is

a. 3 pV/M

b. pV/M

c. M/3 pV

d. 3 PV/M

e. none of these

19. The internal energy of a gas (U) of pressure p, occupying volume V is

a. (3/2) PV

b. (1/2) pV

c. (1/2) pv

d. (1/3) pV

e. none of these

20. High winds of hurricane that damaged Purto Rico in 2017 is due to

a. the large mass of the gas particles

b. the high temperature of the gas particles

c. high kinetic energy of the gas particles

d. larger volume of the gas particles

e. none of these

2.13 Self Test Key

1. a, 2. b, 3. a, 4. b, 5. c, 6. d, 7. b, 8. c, 9. a, 10. b, 11. e, 12. b, 13. c, 14. a, 15. d, 16. e, 17. c, 18. a, 19. d, 20. c.

2.14 Problems

1. If a particle of mass ‘m’ is moving perpendicular to the wall with a velocity ‘v’ and hits the wall as a perfectly elastic collision, what is the change in momentum of the particle? (Ans. – 2 mV)
2. A mixture of ideal gases contains n_1 moles of component 1, n_2 moles of component 2, and occupies volume V, what is the pressure exerted by the mixture? (Ans. $(n_1+n_2)RT/V$)
3. If an ideal gas occupies 24.93553 liters of volume at 100 kPa and 300 K, what is the number of moles of gas? (Ans. 1.0 mol)
4. What is the average time required for a perfume molecule (vapor) of M = 0.1 kg/mol to travel a distance of 5 m at room temperature (T = 300 K)? (Ans. 0.02 s)
5. What is the mean squared velocity for one mole of helium gas at standard temperature and pressure? (Ans. 3.404×10^{12} m^2/s^2)

6. What is the enthalpy of 1.25 mol of an ideal gas at 300 K? (Ans. 7.79 kJ)
7. What is the internal energy of 28 g of nitrogen, if it is assumed to be an ideal gas, at 350 K? (Ans. 8.73 kJ)
8. Design an experiment to measure the molecular velocities.

Chapter 3. The Gas Laws

After completing this chapter, you will be able to:

- Recognize the empirical gas laws, Boyle's law, Charles' law, pressure law, Graham's law of diffusion, etc.,
- Analyze of Charles' law to gain insight into the absolute scale for the temperature.
- Synthesize the ideal gas law from the empirical gas laws.
- Evaluate the applications of the gas laws to chemical reactions and daily events. Evaluate the effect of gravitational field on gas pressure and synthesize the barometric distribution law.
- Examine how the pressure decreases with the height of gas column, the temperature and the molecular weight of the gas.
- Evaluate the composition of a gas mixture as a function of height of the gas column.

Goals

- Examine the properties of gases in terms of pressure, volume, mass, and temperature.
- Examine Boyle's law, Charles' law, Avogadro's hypothesis, Graham's law of diffusion, and deduce ideal gas law by combining these empirical relations.
- Arrive at the absolute scale of temperature by extrapolation of experimental measurements on gases. Examine the properties of gases in terms of their dependence of pressure on height or take into account the effect of gravity on gas pressure.
- Expand our expression for pressure by adding the potential energy of the gas particles in a gravitational field.
- Examine the proportion of oxygen in the air at sea level *vs* on top of Mount Everest.
- Derive the barometric distribution law.

3.1 Why Study this?

As mentioned earlier, gases are by far the simplest substances to investigate and study. This is one of the reasons gas properties have been thoroughly examined for hundreds of years, and these experimental data were initially quantified as empirical laws. Only after the development of the kinetic theory of gases, the intricate connections among these laws were revealed. Our experimental studies of gases continue even today for a variety of applications in meteorology, combustion, weather, reaction dynamics, and exotic states of ultra-cold gas atoms. Our understanding and quantification of the bulk properties of gases are critical for numerous practical applications wherever gases are used, as in daily life, industrial applications as well as in space research. Modeling of gas properties described in the previous chapter comes in handy in explaining a large set of empirical laws that will be described here. In this chapter, we will discuss the kinetic theory of gases and provide a solid basis for applications in the real world.

Since each gas particle has a finite mass, it must be subjected to the laws of gravity. This gravitational attraction can alter the pressure exerted by the gas particles as gas particles above can influence the particles below. Thus, as we move up a skyscraper in an elevator, we feel the drop in pressure and the ears pop. What is this effect due to and how much of a pressure drop occurs for the unit distance we climb? This effect is also important for passengers traveling on a jet and the cabin needs to be pressurized to offset the drop in the pressure as the jet climbs into the sky. Thus, the effect of gravity on the gas pressure is a day-to-day issue, if you are a professional pilot and it is vital for the airline industry. Jets need to be built to withstand this pressure differential so that the doors do not blow out, for example. Thus, practical applications of our daily lives require a quantitative understanding of the effect of gravity on gas pressure.

3.2 Boyle's Law

For an early historical perspective on this topic, the reader is recommended to visit online sources.[1] Gases are elastic, in the sense that when they are compressed like a spring, the gas can expand spontaneously when the force of compression is relaxed. Early observations of this kind of behavior of gases were explained by Boyle's law. This law solidifies the relationship between the pressure and volume of a gas sample at constant temperature for a given mass of the gas. Thus, the empirical relation published in the 17th century states that pressure and volume of a gas are inversely related, or that the product of pressure (p) and volume (V) is a constant when the mass and temperature of the gas are kept constant. Mathematically, we write the equation below, where C is a constant which is related to the gas mass and temperature.

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[1] Boyle's original paper: R. Boyle, *A Defence of the Doctrine Touching the Spring and Weight of the Air*, … (London, England: Thomas Robinson, 1662). Available on-line at: Spain's La Biblioteca Virtual de Patrimonio Bibliográfico. Historical accounts of Boyle's law can be found here: Henry Power, *Experimental Philosophy, in Three Books* … (London, England: Printed by T. Roycroft for John

$$p\,V = C \text{ at constant temperature and mass}$$

An animation from Wikipedia is shown above in Figure 3.1A on the left side. A gas sample is enclosed in a cylinder with a piston, and this is immersed in a temperature bath (blue), which is kept at a constant temperature with the flame underneath. There is a temperature gauge and a pressure gauge to measure these parameters, and we can add or subtract the mass of the gas by injecting extra gas. Thus, we have the means to monitor all four bulk properties of the gas sample. For this experiment, we keep the mass of the gas and temperature constant.

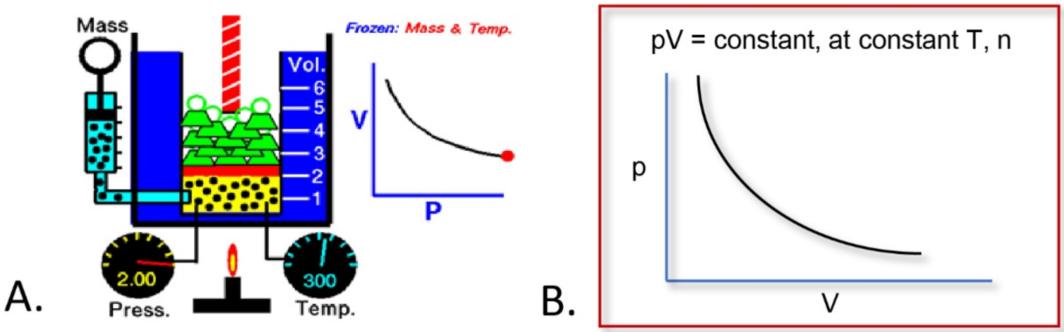

Figure 3.1 Boyle's law experiment. A. A finite mass of a gas is maintained in a cylinder at a constant temperature (blue bath, monitored with a thermometer). Pushing down on the red piston reduces gas volume (V) with a concomitant increase in its pressure (p), as recorded by the pressure gauge. Note that the gas mass and temperature are kept constant. When the piston is allowed to move up by removing the weights on the piston (green blocks), the gas expands, and volume increases. For the animated form of this cartoon, visit Wikipedia.[2] B. On the right, the plot of pressure as a function of volume at constant temperature and gas mass is given, as described by Boyle's law.

Now as we compress the gas by pushing the piston down, the volume will decrease. The converse is true when the gas is allowed to expand by removing the weights on the piston (green). This animation can be viewed on Wikipedia and quite impressive.[2] These observations are then plotted as pressure (p) versus volume (V), as shown on the right (Figure 3.1B) and are described as follows.

The experimental observations support the following description. If we plot gas pressure on the Y-axis and the corresponding gas volume on the X-axis, we get the black curve, at the constant temperature and mass for a given gas. As we move towards the right on the volume axis, the volume is increasing, and the pressure drops smoothly. This is the process of expansion. Conversely, as we move along the volume axis towards the left, we are reducing the volume and the pressure of the sample rises. This is the process of compression. Thus, we can either increase the pressure of the gas and reduce its volume or decrease the pressure of the gas and allow it to expand.

Notice that Boyle's law applies approximately to all gases, independent of their chemical composition. If we were to make these pressure-volume measurements very precisely at a variety of temperatures, then we would see that our data deviates from what is predicted from this law. Strictly speaking, this law is obeyed only by an ideal gas but can be roughly applied to real gases. This means our expectation of pV being

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Martin and James Allestry, 1663), pp. 126-130. Available online at Early English Books Online (https://quod.lib.umich.edu/e/eebo/a55584.0001.001/155?page=root;size=125;view=text).

[2] Boyle's Law diagram created by Glenn Research Center available at https://www.grc.nasa.gov/WWW/K-12/airplane/boyle.html, Public Domain. More information available at https://en.wikipedia.org/wiki/Boyle%27s_law.

constant is not valid in most cases, and we should expect the value of the constant to change. This aspect will be discussed in later sections. For now, we will be content with Boyle's law as an approximate description of the real gas behavior but describes ideal gas behavior accurately.

3.2.1 Molecular interpretation of Boyle's law

The kinetic theory of gases provides a molecular interpretation of Boyle's law as well. For example, as we increase the volume of the gas, the particles will be traveling long distances before colliding with the wall but this does not affect their velocity or their momentum of impact. But this increases the round-trip time our particle takes between successive collisions. Thus, the frequency of collisions with the wall decreases, and hence the rate of change of momentum decreases. This, in turn, decreases the force exerted by the particle on the wall, and hence, the pressure exerted by each particle decreases. Thus, the total pressure exerted by the gas decreases with an increase in volume at constant temperature and mole numbers. Thus, we can readily understand Boyle's law using the descriptions of the kinetic theory of gases. This kind of molecular level detail is essential in understanding modern chemistry.

3.3 Charles' Law

The relation between the temperature and volume of the gas at constant pressure and gas mass is given by Charles' law, the law of thermal expansion of gases. Early historical perspectives of this law can be found here.[3] The volume of a gas increases linearly with temperature, and the gas expansion coefficient was found to be constant for all gases. Consider the earlier example of a finite mass of gas held in a cylinder with a piston, equilibrated in a thermal bath (Figure 3.2A). You may go to Wikipedia[4] to examine the animation that goes with this graphic for a better understanding of the effect of temperature on the volume of the gas. When the temperature of the bath is raised by heating with a flame underneath and the gas is held at constant pressure, the gas volume increases, and the piston gets pushed up. The volume increase depends linearly on temperature (Figure 3.2B). The temperature is still being measured in Centigrade (t).

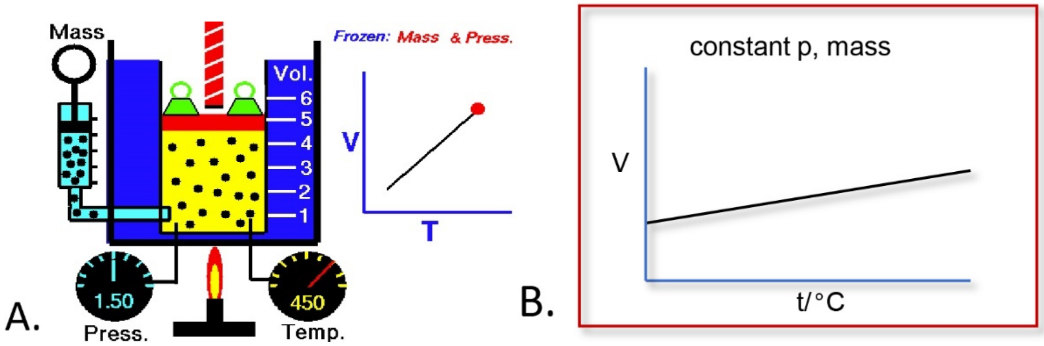

Figure 3.2 Charles' law experiment. A. A finite mass of a gas is maintained in a cylinder at a constant pressure. As the temperature (blue bath, monitored with a thermometer) is increased, the red piston rises, and the gas volume (V) increases. For an animated form of this cartoon, visit Wikipedia.[5] B. Plot of volume as a function of temperature at constant pressure and mass is given, according to Charles' law.

A plot of volume (V) measured as a function of temperature (t) is nearly linear for most gases, as shown in Figure 3.2B. The above observation was used to construct a 'Volume' thermometer. That is, a sample of gas is enclosed in a container, held at constant pressure, and volume is measured at various temperatures. Since volume is allowed to vary while the pressure is held constant, it is referred to as a Volume (or constant pressure) thermometer. This device played a very important role in understanding the nature of temperature and formed a foundation to establish the absolute scale of temperature.

The above plot has a finite intercept (V_o) at t = 0 and has a slope given by the first derivative of volume with respect to temperature. Therefore, we can write,

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[3] Gay-Lussac, J. L. *(1802), "Recherches sur la dilatation des gaz et des vapeurs" [Researches on the expansion of gases and vapors], Annales de chimie,* ***43****: 137–175.* English translation (extract).

[4] Animation for Charles' law can be found here: https://en.wikipedia.org/wiki/Charles%27s_law

[5] https://en.wikipedia.org/wiki/Charles%27s_law. NASA's Glenn Research Center
- http://www.grc.nasa.gov/WWW/K-12/airplane/aglussac.html. Public Domain.

$$V = V_o + \left(\frac{\partial V}{\partial t}\right)_p t$$

where the slope ($\left(\frac{\partial V}{\partial t}\right)_p$) and intercept ($V_o$) are given explicitly.

This equation can be written in a more convenient form by dividing the slope with the intercept so that the degree of expansion per unit volume is obtained, and the corresponding slope will be independent of the initial volume and more convenient to compare data from different experiments. Dividing the above with V_o we get,

$$V / V_o = 1 + (1/V_o)\left(\frac{\partial V}{\partial t}\right)_p t$$

$$\text{by definition, } (1/V_o)\left(\frac{\partial V}{\partial t}\right)_p = \alpha_o$$

Where α_o is the coefficient of thermal expansion per unit volume, and the numerical value is (1/273.15) which is the same for all gases, independent of their chemical composition. This is another breakthrough in our understanding of matter.

Example 3.1

For one mole of helium gas at standard pressure and temperature (p = 1 atm; V = 22.4 liters at 0 ˚C), what is the coefficient of thermal expansion for helium?

The value of the thermal expansion coefficient for helium is (1/273.15)/˚C, which is the same for all gases [$\alpha = (1/V)(dV/dT)_p = (1/V)(nR/p) = 1/T$.

We next write the above equation by substituting various values. We will do one more manipulation to convert degrees Celsius into the absolute scale of temperature, as follows.

$$V / V_o = 1 + \alpha_o t$$

$$V = V_o + V_o \alpha_o t$$

By multiplying and dividing the right side with α_o, we get

$$V = V_o \alpha_o (1/\alpha_o + t)$$

$$V = V_o \alpha_o (273.15 + t)$$

$$V = V_o \alpha_o T$$

at constant pressure and mass, where T = 273.15 + t, defined as the absolute scale of temperature or the Kelvin scale of temperature.

Example 3.2

What is the coefficient of thermal expansion of helium (ideal gas) at standard pressure and temperature (p = 1 atm; V = 22.4 liters at 0 ˚C), and what is the increase in the coefficient with temperature, at constant volume and mass? Comment on how it may or may not change from one ideal gas to another.

The coefficient the coefficient of thermal expansion is (nR/pV) and thus, it decreases with an increase in temperature but independent of the nature of the ideal gas (molar mass).

3.3.1 The absolute scale of temperature

One major revelation from Charles' law is that it provided an extraordinary insight into the absolute lower limit for the temperature in the universe, and it allowed for the recognition of the absolute temperature scale. Initially, the temperature of an object is measured relative to that of the ice bath or another standard, and therefore, the temperature scale was relative to a chosen standard. This is perfectly fine for most purposes, we still use these scales of temperature in our daily lives, but temperature can be defined on an absolute scale. This latter definition provided a unique insight into the nature of temperature and the lowest possible temperature that could ever be obtained. This is similar to the velocity of light being the absolute upper limit in the universe. Thus, simple laboratory experiments allowed us (humans) to recognize certain absolute limits the universe imposes.

The temperature on the absolute scale is denoted by 'T' distinguishes it from the traditional Centigrade or relative temperature scales which are denoted by 't'. The absolute scale of temperature can be arrived at by analyzing Charles' law plot of V vs. t (Figure 3.3). Consider an extrapolation of the straight line shown in Figure 3.2 B till it cuts the X-axis at the negative value of the temperature scale. Since the volume of gas cannot be reduced to zero, or a negative quantity, one concludes that this is the lower limit for the temperature of the universe! This is the reason the temperature scale based on this lower limit (T=0) is the absolute scale of temperature or the Kelvin scale of temperature (K, kelvin).

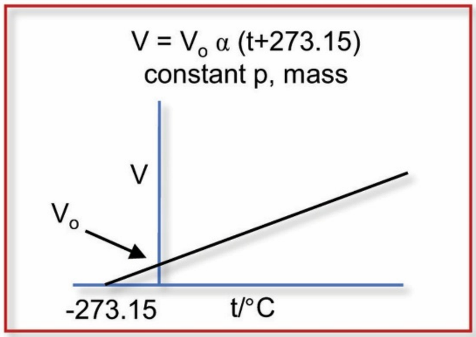

Figure 3.3 Absolute scale of temperature is defined using the prediction of Charles' law that there is an absolute limit to the lowest possible temperature, being -273.15 ˚C or T = 0. This is the intercept on the temperature axis when V = 0. Further reduction in temperature will have to produce a negative volume for the gas which is not possible. Thus, this is the lower limit for temperature that could ever be achieved.

A clear understanding and interpretation of Charles' Law leads us to an interesting extrapolation about the lowest temperature one can achieve and this turns out to be a very profound and important conclusion in physical chemistry. Kelvin has concluded that this is the lowest temperature that is ever attainable anywhere in the universe. Thus, it formed a natural lower limit for the definition of a new scale of temperature, the absolute scale because it does not depend on any arbitrary reference point. So far, our efforts have resulted in achieving few tens of micro kelvin (μK) as the lowest temperature ever achieved in the lab. The degree symbol is not used here, because it is the absolute scale of temperature, unlike Centigrade (˚C) or Fahrenheit (˚F), which use ice (freezing) point and boiling point of water to define the temperature scales.

3.3.2 Molecular interpretation of Charles' law

As the temperature of the gas is increased, gas molecules have greater thermal energy and since, they do not have any potential energy (by definition ideal gas no interactions between particles and hence, has no potential energy) all this energy is kinetic energy (0.5 m $<c^2>$). Then, the increase in kinetic energy implies an increased velocity of the gas particles because the mass of the particle (m) is constant. Thus, an increase in gas temperature allows them to travel at greater velocities, on average. Increased velocity increases the momentum, which in turn increases the rate of change of momentum when it collides with the wall. Thus, the force exerted by the particles on the container walls also increases. If we do not constrain the volume, the gas pushes the piston up, occupying more volume. Thus, an increase in temperature increases gas volume when the pressure and mass of the total gas in the container are kept constant.

3.4 Pressure Law of Gay-Lussac

Since the volume of a gas is a function of temperature (Charles' law) at constant mass and pressure, we apply Boyle's law at each temperature point and conclude that the pressure should also be a linear function of temperature. This relationship between pressure and temperature, at constant volume and gas mass, was observed by Gay-Lussac and termed as the pressure law.

$$\mathrm{p} \propto \mathrm{T} \quad \text{or} \quad \mathrm{p/T} = \text{constant}$$

A plot of pressure vs. temperature should be linear with an intercept of zero.

3.4.1 Molecular interpretation of the pressure law

Expanding on the kinetic theory of gases, we recognized earlier that increasing the temperature increases the kinetic energy of the gas particles. However, when the volume of the container is constrained to be constant, then the gas particles travel the same average round-trip distance between successive collisions but the momentum carried by each particle is now higher. Thus, each collision applies a greater amount of force on the container wall and the number of collisions per second is also increased as the particles travel faster at higher temperatures. Thus, the force exerted on the wall is increased with an increase in temperature, and hence, the gas exerts higher pressure at higher temperatures when we hold the volume constant, for a constant mass. Thus, all the above empirical gas laws discussed thus far, can be explained based on a molecular level understanding and by applying classical mechanics.

3.5 Law of Combining Volumes of Avogadro

So far, we have discussed the relationship between, volume, temperature, and pressure, and one remaining property of gases is their mass. The relation between the mass and other properties of the gas is given by the law of combining volumes or Avogadro's hypothesis, discussed below.

Avogadro's hypothesis is considered to be the beginning of the atomic/molecular theory. Since chemical substances (gases as an example) combine in finite proportions, Avogadro hypothesized that equal volumes of different gases should contain the same number of particles at constant pressure and temperature. In other words, the number of particles in a gas sample is proportional to its volume at constant pressure and volume. This is obvious in the case of pure gas. If we double the number of particles of the gas, at constant p and T, then its volume should also double.

However, this is less clear when we compare different gas samples. Avogadro hypothesized that if we have a gas with a certain volume (V_1) with a certain number of gas particles (N_1) as well as a second gas sample that has a volume V_2, with N_2 number of particles (both at same constant T and p), then it is mandatory that $V_1 / V_2 = N_1 / N_2$. If $V_1 = V_2$ then N_1 must equal N_2.

The experimental data indicates that one volume of nitrogen reacts completely with three volumes of hydrogen to give two volumes of ammonia.[6] All volumes are measured at standard temperature and pressure. Thus, the stoichiometry for this reaction is as given in Figure 3.4. This leads to an important concept in chemistry; the law of combining volumes. For example, if each volume contains the same number of particles, then one particle of nitrogen must react with three particles of hydrogen to produce two particles of ammonia (Figure 3.4). We obey the law of conservation of mass and hence, the total mass remains the same except for any heat release or absorption during the reaction. Contrary to popular misconception, any energy changes that occur during a chemical reaction are to be accounted for by using Einstein's mass equivalence equation. But this change in mass in most chemical reactions is negligible for all practical purposes.

Thus, 28 g of nitrogen reacts with 6 g of hydrogen to give 34 g of ammonia, and this has been confirmed experimentally. The formula weights of the substances match this ratio, and hence, two particles of ammonia are produced from 1 particle of nitrogen and 3 particles of hydrogen. This observation can be explained only when each volume of the gas contained the same number of particles. This is the reason it is a hypothesis that was proposed and later confirmed to be true. This hypothesis formed the modern foundation for the concepts of mole, molecular weight, stoichiometry, and the atomic theory.

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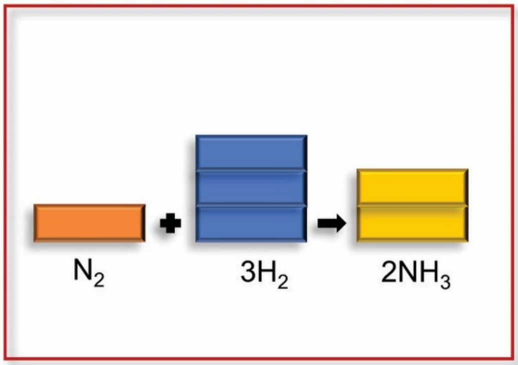
[6] James, Laylin K. (1993). *Nobel Laureates in Chemistry 1901–1992* (3rd ed.), Washington, DC: American Chemical Society. p. 118.



$$N_2 + 3H_2 \longrightarrow 2NH_3$$

Figure 3.4 Chemical substances (gases) combine in finite volumes. One volume of nitrogen gas, for example, reacts completely with three volumes of hydrogen gas to give two volumes of ammonia gas, all volumes measured at standard temperature and pressure. If we fix the mass of one volume of hydrogen as 2 g (arbitrarily), then we find that 28 g of nitrogen (1 mol) reacts with 6 g (3 mol) of hydrogen to produce 34 g (2 mol) of ammonia (approximately). Total mass should be the same before and after the chemical reaction (law of conservation of mass/energy).

If we fix the mass of one volume of hydrogen to be equal to 2 g as a standard and state that it contains one mole of hydrogen molecules, then three moles of hydrogen react with one mole of nitrogen to produce two moles of ammonia. Then 6 g of hydrogen or 3 mols, 3 Volumes react with 28 g or 1 mol, 1 V of nitrogen to produce 34 g or 2 mols or 2 volumes of ammonia. Then, from the above stoichiometry, we conclude that three moles of hydrogen weigh 6 g, or one mole of nitrogen weighs 28 g, and two moles of ammonia weigh 34 g. If we fix the molecular weight of hydrogen as 2=6/3, then the molecular weight of nitrogen must be 28 28/1, and that of ammonia 17=34. Note that molecular weights are ratios of the weight of one mole of the substance to that of the hydrogen and have no units. Thus, we fix that one mole of hydrogen weighs 2 g, nitrogen 28 g, and so on, under standard conditions. Thus, the concept of mole resulted in the definition of molecular weights.

By convention, at standard temperature and pressure, 1 mole of hydrogen weighs 2 g, or 1 mol of carbon weighs 12 g and both contain an Avogadro number of particles. This is a convenient choice and agrees with the atomic number of the elements, one could have chosen any weight of any element to define the mole. It gives the relation between the mass of a gas, mole numbers, volume, temperature, and pressure. The concept of the mole was born.

To follow chemical reactions, we need to follow the number of particles or mole numbers, instead of the masses of substances. The number of particles can be converted to grams by using the corresponding atomic weights or molecular weights. Thus, the basic concepts of chemistry are intertwined with this central hypothesis. The concept of mole in chemistry is very important as it centers on the most fundamental understanding of how molecules and atoms react in finite proportions.

Example 3.3

One mole of helium gas at standard pressure and temperature, $p = 1$ atm; $V = 22.4$ liters and 0 ˚C weighs 4 g. Calculate the number of particles in it.

One mol of helium contains an Avogadro number of particles (6.02214×10^{23}), under any conditions.

3.5.1 Molecular interpretation of Avogadro's hypothesis

Let us say that two gas different samples of particle masses m_1 and m_2 occupy the same volume, have average speeds $<c_1^2>$ and $<c_2^2>$ at the same pressure (p) and temperature (T) but also have a different number of particles (N_1 and N_2). Since their pressure and volume are the same, then $pV = 1/3\ N_1 m_1 c_1^2 = pV = 1/3\ N_2 m_2 c_2^2$). Since the two gases are at the same temperature, their kinetic energies must be equal or $m_1 c_1^2 = m_2 c_2^2$. Then we conclude that N_1 should be equal to N_2.

3.6 The Ideal Gas Law

One can deduce the overarching relationship among pressure, volume, temperature, and mass of a gas by combining Boyle's Law, Charles' law, and Avogadro's hypothesis. For example, from Boyle's law, at a constant temperature, we have

$$pV = C$$

where p is the pressure, V is the volume, and C is a constant. Since equal volumes contain an equal number of particles as stated by Avogadro's hypothesis, volume is proportional to the mole number, and hence, C can be replaced by nD where n is the number of moles of the gas, and D is a new constant.

$$\mathrm{pV = nD}$$

From Charles' law, we note that V is proportional to T, at constant pressure and mass, and hence we can write the new equation with another proportionality constant R as,

$$\mathrm{pV = nRT} \text{ (Ideal gas equation)}$$

Now, all that we need to do is to figure out what R is. We can do so by substituting the volume occupied by 1 mole of any gas (22.4 liters) under conditions of pressure (1 atm) and temperature (273.15 K).

Example 3.4

For one mole of an ideal gas at standard temperature and pressure, we have p = 1 atm; V = 22.4 L, and n = 1. Calculate the gas constant, R.

R = pV/nT; T= 0+273 K, thus, R = (1 atm*22.4 L)/(1 mol*273 K)

R is the 'Gas constant' in the above equation and with the ideal gas equation, pV = nRT, we can readily write Boyle's law, Charles' law, and Gay-Lussac law. It's called the ideal gas law because only ideal gas follows this equation exactly, but real gases also obey this equation approximately. Throughout our studies of thermodynamics, we will generally assume that we are using ideal gases only unless stated otherwise.

Table 3.1 Values for the gas constant

Value	*Units*	*Value*	*Units*
8.3145	$\mathrm{J\ K^{-1}\ mol^{-1}}$		
8.3145	$\mathrm{m^3\ Pa\ K^{-1}\ mol^{-1}}$	62.364	$\mathrm{L\ Torr\ K^{-1}\ mol^{-1}}$
8.3145	$\mathrm{kg\ m^2\ s^{-2}\ K^{-1}\ mol^{-1}}$	1.9872	$\mathrm{kcal\ K^{-1}\ mol^{-1}}$
8.3145	$\mathrm{erg\ K^{-1}\ mol^{-1}}$	0.0821	$\mathrm{L\ atm\ K^{-1}\ mol^{-1}}$
8314.5	$\mathrm{L\ Pa\ K^{-1}\ mol^{-1}}$	8.31	$\mathrm{kg\ m^2\ K^{-1}\ mol^{-1}}$

Example 3.5

One mole of helium gas at p = 1 atm; V = 22.4 liters and t = 0 ˚C weighs 4 g. Calculate the gas constant in units containing grams.

R (helium) = pV/nT = (1 atm 22.4 L) / (4 g 273.15 K) = 8.314 (J/mol)(mol/4 g) $\mathrm{K^{-1}}$ = 2.078 J $\mathrm{g^{-1}\ K^{-1}}$.

In summary, we have described specific properties of gases (p, V, n, and T) in terms of the above empirical equations and argued that learning about gases could be useful for our discovery of thermodynamic laws, the basic laws that govern the universe!

3.6.1 Molecular interpretation of ideal gas law

Using molecular descriptions, we already showed that $pV=(1/3)Nm<c^2>$ and by inferring that all energy of the gas is only kinetic (no potential energy because the particles do not attract or repel each other), we deduce ideal gas law. Since the kinetic energy of the ideal gas is (1/2) m $<c^2>$, we can write pV = N B T where B is a proportionality constant. If we choose n moles of the substance, we can write n= N/N_A where N_A is the Avogadro's number, or pV = n N_A B T. Above, we defined that R = pV/nT and hence, R = N_A B or we get pV = nRT, the ideal gas law. Thus, through molecular descriptions alone, we arrive at the ideal gas law.

3.7 Dalton's Law of Partial Pressures

Chemical reactions involving gases often contain mixtures of gases. They could be a mixture of reactants before the reaction or mixtures of reactants and products when the reaction is proceeding, or the products could also form a mixture. Thus, we need to examine the mixing of gases and study how gas mixtures behave when compared to pure gas. This inquiry leads us to the concept of partial pressure.

Let there be pure gases of volumes V_1, V_2, V_3, V_4… V_i with the corresponding mole numbers n_1, n_2, n_3, n_4…n_i, respectively, at a certain temperature T (Figure 3.5). We assume that these are ideal gases and that the gases do not react. Then, when mixed at constant pressure and temperature, the total volume (V_t) equals the sum of all the individual volumes ($\sum V_i$). The total mole number (n_t) equals the sum of all the individual mole numbers ($\sum n_i$) because of the law of conservation of mass. Since we have ideal gases, the total pressure of the mixture (p_t) is n_tRT/V_t. This leads us to the concept of partial pressure.

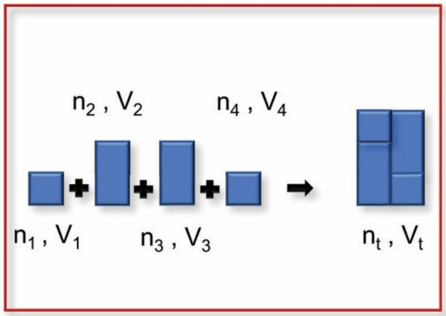


Figure 3.5 Pure gases of certain volumes and mole numbers (left) are mixed at constant temperature and pressure. If the gas samples do not react with each other, then the total volume of the gas mixture (right) is the sum of individual volumes and the total mole number is the sum of individual mole numbers.

3.7.1 Partial Pressure

The partial pressure of a gas component in a mixture is the pressure exerted by that component when it occupies the entire volume by itself, and therefore, it is equal to the number of moles of that substance (n_i) multiplied by RT and divided by the total volume (V_t), or n_iRT/V_t. Since the mole number of the component is less than the total mole numbers, the partial pressure of a substance must be less than the total pressure. Since mixing of gases at constant pressure requires adding the volumes together, the partial pressure of a gas component in the mixture is also less than its initial pressure, before mixing.

3.7.2 Total pressure and partial pressure

Dalton's law states that the total pressure (p_t) of a mixture of gases that do not react is equal to the sum of the partial pressures (p_i) of the individual gas components, the total pressure of the mixture, p_t is given as,

$$p_t = p_1 + p_2 + p_3 + p_4 + \dots$$

This equation is readily deduced by simple mathematical transformations, as shown below.

Total number of moles of the mixture is the sum of the mole numbers, $n_t = n_1 + n_2 + n_3 + n_4 + \dots$

Total volume of the gas mixture is the sum of the component volumes, $V_t = V_1 + V_2 + V_3 + V_4 + \dots$

Total pressure of the gas mixture in terms of total mole numbers and total volume is shown below.

$$p_t = \frac{n_tRT}{V_t} = \left(\frac{n_1 + n_2 + n_3 + n_4 + \dots}{V_t}\right) RT$$

$$p_t = \frac{n_1RT}{V_t} + \frac{n_2RT}{V_t} + \frac{n_3RT}{V_t} + \frac{n_4RT}{V_t} + \cdots$$

Thus, we arrive at the Dalton's law of partial pressures where the partial pressure is summative. This leads us to the concept of mole fraction.

3.7.3 Mole fraction

Further, the partial pressure of a gas component is also related to its mole fraction, (x_i) and the mole fraction of a component is the ratio of the number of moles of the particular component (n_i) to the total number of moles in the mixture (n_t), as shown below.

$$x_i = \frac{n_i}{n_t} = \frac{\frac{p_i V_t}{RT}}{\frac{p_t V_t}{RT}} = \frac{p_i}{p_t}$$

We replace the mole numbers with the respective pressure-volume terms using the ideal gas law. Next, we cancel the total volume and temperature terms from the denominator and the numerator. The net result is that the mole fraction is equal to the ratio of the partial pressure to that of the total pressure. By rearranging, we see that the partial pressure of a given component is equal to the mole fraction of that component multiplied by the total pressure.

$$p_i = x_i \, p_t$$

Because the partial pressure of the gas is proportional to its mole fraction, the partial pressure of each gas component can be calculated with the total pressure and the corresponding mole fraction.

Example 3.6

A mixture of one mole of helium and one mole of hydrogen is at a total pressure, p_t = 1 atm occupying a total volume of V_t = 50 liters, in a weather balloon. Calculate the mole fraction of helium and its partial pressure in the balloon.

X (helium) = (1/1+1) = 0.5. Partial pressure of helium in the mixture = 1 atm x 0.5 = 0.5 atm

3.7.4 Molecular interpretation of partial pressure

The partial pressure of a component of a gas mixture is related to the amount of pressure that the component exerts on the walls of the container. Thus, when we sum the total pressure exerted by the gas, we only will count the number of particles of the particular component, and we are not interested in the rest of the components. Thus, partial pressure is the pressure exerted by that component that is of interest to us. Naturally, the sum of the partial pressures of the components equals the total pressure because we sum the number of particles of each component to get the total number of particles in the mixture, and so, we sum the pressure exerted by each component to get the total pressure. Similarly, the partial pressure of a given component is proportional to its mole fraction.

3.8 Molecular Weight Measurements

The determination of molecular weights of gases has been a significant problem at the beginning of chemistry. The kinetic theory of gases provided a simple method to determine these important quantities. Using ideal gas law, we can relate the molar mass of the gas with gas density. First, we recognize that the number of moles (n) is given as the gas mass (w) divided by its molar mass (M), we can replace n in the ideal gas law and rearrange to obtain M.

$$pV = nRT = (W/M)\ RT$$

$$M = (W/V)\ (RT/p)$$

We recognize that W/V is density (ρ), write M in terms of density in the following manner.

$$M = (\rho)\ (RT/p) = (\rho RT/p)$$

$$\rho = pM/RT$$

By simply measuring the density of a gas sample (mass and its volume), we can calculate its molar mass (Figure 3.6), an extraordinarily simple result!

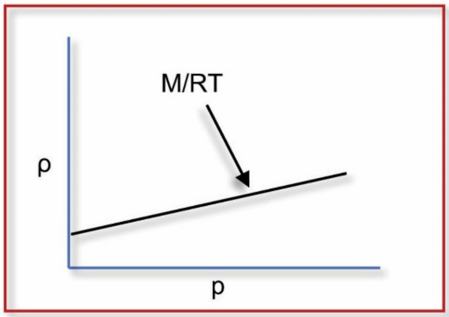


Figure 3.6 Molecular weights or molar masses of gases can be obtained by measuring their density as a function of pressure, at constant volume and temperature. A gas cylinder of known volume can be charged with a pure gas at increasing pressures (constant volume) and its weight measured accurately to estimate molar mass using the relation $M = \rho RT/p$. A plot of p versus density gives a straight line with a slope equal to M/RT and knowing R and T, we obtain M.

So, we measure the density of a given gas at different pressures at constant temperature and volume. A plot of density, ρ versus pressure, p should give a linear plot (Figure 3.6) and the slope of the line should be equal to M/RT. That is how early measurements of molar masses of simple, volatile substances were measured, and often volatile liquids and solids were converted to vapors and their molar masses determined by this method.

Example 3.7

Given the molar mass of water vapor at 25 ˚C and 1 atm is 18 g/mol, what is its vapor density?

Density of water vapor at 25 ˚C (assuming ideal behavior) = pM/RT = (1 atm 18 g/mol)/(R 278.15 K). Using R = 0.082057 atm L mol^{-1} K^{-1}, we get the estimated density as,

ρ = (1x18 atm g/mol)/(0.082057 atm L mol^{-1} K^{-1} 278.15 K) = 18/(0.082057x278.15) g/L = 0.7844 g/L

We also recognize that most real gases do not exactly obey the ideal gas law. Therefore, the molecular masses we measure using this approach will have a certain amount of error. More accurate molar masses are obtained routinely by mass spectrometry.

3.8.1 Molecular interpretation of molar mass

Molar mass is related to the mass of the gas particles, and by definition it is the mass of Avogadro number of particles. Therefore, the molar mass is proportional to gas pressure at constant temperature and volume. Thus, this kind of insight is obtained from the kinetic theory of gases. Molecular description of the gas is essential to link various equations obtained thus far.

3.9 Graham’s Law of Diffusion

Molar masses were also measured by measuring the diffusion of gases through a porous membrane through the application of Graham’s law of diffusion. Experimental observation has been that the rate of diffusion of a gas sample through a porous plug is inversely related to the square root of its density. The diffusion rate is the movement of particles across a unit area of cross section in unit time. Diffusion can occur in the gas, liquid, or even in the solid phase. An excellent animation of this and other gas laws can be found here.[7]

Initially, Graham established that the rate of diffusion is inversely proportional to the square root of the density of the gas, and several years later he published the new relation connecting the rate of diffusion to the molar mass. In the previous section, we recognized the relationship between the density and molar mass of the gas, and thus, we can readily see how both the laws are related. By comparing the diffusion rates of two gases, we can determine their relative molar masses.

$$\text{rate of diffusion} \propto \sqrt{1/\text{density}} \text{ or } \sqrt{1/\text{molar mass}}$$

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[7] https://courses.lumenlearning.com/boundless-chemistry/chapter/diffusion-and-effusion/

$$\frac{\text{Rate 1}}{\text{Rate 2}} = \sqrt{\frac{\text{Density 2}}{\text{Density 1}}} = \sqrt{\frac{\text{Molar Mass 2}}{\text{Molar Mass 1}}}$$

In addition to diffusion, another process called ‘effusion’ is also examined. Effusion is the leakage of gas molecules through a small opening, like diffusion except that the flow is via a small opening instead of a porous plug. The diameter of the opening is to be smaller than the distance the particles travel between an average of successive collisions (the mean free path).

Example 3.8

Calculate the ratio of the rates of diffusion of hydrogen to oxygen and predict how many times faster hydrogen will effuse through an opening when compared to oxygen.

$$\frac{\text{Rate for hydrogen}}{\text{Rate for oxygen}} = \sqrt{\frac{\text{Molar Mass of oxygen}}{\text{Molar Mass of hydrogen}}} = \sqrt{\frac{32}{2}} = 4$$

Thus, hydrogen will effuse four times faster than oxygen.

The rate of effusion of a gas is also proportional to the square root of its molar mass. For example, if we have a mixture of hydrogen and oxygen and the gas is allowed to leak through a small opening, then as the gas leaks out, the mixture is gradually enriched in oxygen. This is because the lighter hydrogen will escape faster than the heavier oxygen. In a later chapter, we will show that the kinetic theory of gases can be used to derive the diffusion coefficient and then derive Graham’s law.

Thus, a simple measurement of gas diffusion or effusion rate will be sufficient to determine the molecular weight of the gas, but the apparatus is to be calibrated with a gas sample of known molecular mass. This law is exploited in gas separations using membranes or diffusers.

3.9.1 Molecular interpretation of Graham’s law

Diffusion is a process that entails the movement of molecules from one region of the container to the other. The diffusion rate depends on the RMS speed of the gas, as particles have to move across the porous plug. Using the kinetic theory of gases, we showed that this is inversely proportional to the square root of particle mass. The lighter the particle, the faster it moves and the greater the diffusion rate.

3.10 The Barometric Law

Imagine that you have a column of gas at sea level, and we ask the question how does the pressure of the air vary as we travel from the surface of the ocean into outer space? We experience that the atmospheric pressure depends on the height, and we would like to know how it varies with height. We use the ideal gas law and figure out how the pressure is related to the height of the gas column.

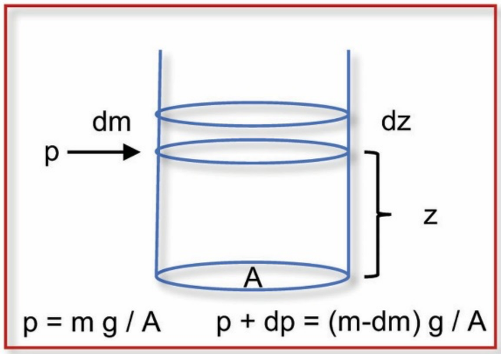

Figure 3.7 Gas column above the sea level with an area of cross section of A, pressure is p at height z and the mass of the gas above this height is m. The pressure exerted at height z is due to the gas mass experiencing the gravitational pull (mg) and continues to decrease as we scale the column.

3.10.1 Derivation

Strategy: We will consider a gas column (Figure 3.7) of area cross section A, under the influence of gravity and compute pressure at any height z due to the gas column above it. The bottom of the column is at a reference where z = 0 and we will assume that the temperature of the gas is the same throughout the gas column, irrespective of its height, or else the derivation gets complicated. Let m be the mass of the gas column above the height z.

The pressure due to the gas column at any height is due to the gravitational force (mass times acceleration due to gravity on earth (g)) at that point divided by the area of cross section (A). We will define pressure to be p at height z and p+dp at height z+dz. We will express dp in terms of dz and integrate the expression to obtain the mathematical relation between height z and pressure p. The following is our mathematical journey.

The pressure p due to mass of the gas m above the height z is mg/A where g is the acceleration due to gravity. Let dm be the mass of gas in the interval dz, then the mass of the gas above the height z + dz will be m – dm, because the mass of gas in the column decreases as we move up the column. We have the following steps.

$$p = mg/A$$

$$p + dp = (m\text{-}dm)g/A$$

Expanding the right side and rearranging the values to obtain dp, because we want to integrate this to get the function of pressure with respect to z, we get the following.

$$dp = (mg\text{-}g\ dm)/A + mg/A$$

$$dp = (mg\text{-}g\ dm - mg)/A$$

$$\text{or}\ \ dp = -\ dm\ g/A$$

We can integrate this expression and get the expression for pressure, but it will relate pressure with mass, not the height. So, we now convert dm in terms of dz. We recognize that the denominator has the area of cross-section and if we multiply this with dz we get volume dV in the denominator. Change in mass with respect to volume is density, and dV = A dz, so we can write the above in terms of dz using this insight, in the following manner.

$$\text{density},\ \rho = dm/dV$$

$$dm = \rho dV = \rho dz\ A$$

Substituting this in the expression for dp above, we get an expression that is suitable for integration.

$$dp = -\ dm\ g/A = -\rho\ dz\ A\ g/A$$

$$dp = -\rho\ g\ dz$$

Integrating the above with limits, we will be able to get the desired expression but for this operation, the density has to be a constant however it is a function of z itself. So, we need to write density also in terms of z to finally get the desired expression for integration.

Previously, we wrote pV = nRT where n is mass of gas (w) divided by its molecular weight (M), and expressed pressure in terms of density, ρ. We will use this to replace density with a function of pressure, as follows.

$$pV = nRT = (w/M)\ RT$$

$$p = (w/MV)\ RT = (\rho/M)\ RT$$

$$\rho = pM/RT$$

Now, we replace density with pressure, as below.

$$dp = -\ \rho\ g\ dz = -\ (pM/RT)\ g\ dz$$

$$(1/\mathrm{p})\ \mathrm{dp} = -\ (\mathrm{Mg/RT})\ \mathrm{dz}$$

We can integrate this expression readily because g, M, R, and T are constants, and we have pressure terms on the left side and dz on the right side. Next, we choose the limits for integration. Let p_o be the pressure of the gas at the bottom of the gas column when z = 0, the lower limit. Let the pressure be p at any height z, as the upper limit. Integration with these limits gives us the following.

$$\int_{p_0}^{p} 1/p\ \mathrm{dp} = -\int_{0}^{z} (Mg/RT)\ \mathrm{dz}$$

$$-\ \ln\,(\mathrm{p}/p_0) = \mathrm{g\,z\,(M/RT)}$$

Converting the logarithmic function into the exponential function, we get the final answer to our question.

$$\mathrm{p} = p_0\ e^{-(MgZ/RT)}, \text{ the Barometric Law}$$

3.10.2 Analysis of the barometric law

We have shown that the pressure of a gas in a gas column decreases with increase in height in an exponential manner and this is the quantitative relationship referred to as the barometric law. Now let's analyze this equation in different ways and try to understand what it is telling us.[8]

3.10.3 Effect of height

A plot of pressure as a function of height shows that the pressure decreases exponentially with the increase in height (Figure 4.2). This is because the height is in the numerator of the exponent and the exponent has a negative sign. Thus, an increase in z decreases the value of the exponent and decreases the value of the pressure calculated by this function. When z = 0, p = p_o, our reference point at the sea level. Many natural processes that we know of, follow this kind of exponential decay law, and we also refer to these as the first order process, but we will learn more about why these are intrinsically exponential in later classes.

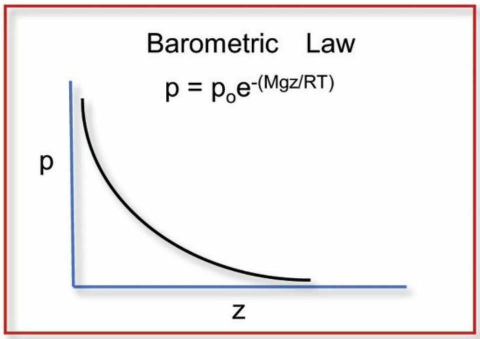

Figure 3.8 Plot of pressure as a function of height predicted by the Barometric law. Pressure drops exponentially with height and thus, air pressure at the mountain top is less than at sea level.

Now we have a good explanation as to why the air thins out as we climb a mountain or as the elevator climbs the floors. The atmosphere becomes thinner and thinner as we climb higher and higher, or it gets denser and denser as we descend due to the gravitational field, and this is the major reason for the drop in the pressure with an increase in height. The exponent in our function also has two other interesting variables, M and T which need further analysis.

Example 3.9

Calculate the pressure at a height of 1 km if our atmosphere consisted of only helium.

Strategy: Simply substitute these values into $\ln(p/p_o) = (Mgz/RT)$, assume the temperature is constant, t = 25 ˚C, use acceleration due to gravity on earth and the atomic weight of helium.

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[8] Berberan-Santos, M. N., The barometric formula, American Journal of Physics **65**, 404 (1997); https://doi.org/10.1119/1.18555

$$\ln\frac{p}{p_0} = -\frac{M\,g\,z}{RT} = -\frac{0.004\,kg\;9.8\,m\;\;1000\,m\,s\,s\,K\,mol}{mol\;\;s\,s\,8.31\,kg\,m\,m\,298.15\,K} = -\frac{4*9.8}{8.31*298.15} = -0.0156$$

Or p =0.98 atm

3.10.4 Effect of temperature

If we were to analyze the influence of height on different planets whose atmospheres are at different temperatures, then how does the pressure drop with height on those planets? This is illustrated in Figure 3.9 where we plot the natural logarithm of pressure (normalized to pressure at the sea level) as a function of temperature. For example, if the temperature is higher, then the denominator in our barometric equation is larger and the value of the exponent decreases. Thus, the exponential will decay slower with an increase in height. Therefore, the slope of the linear plot, - $gz\ (M/R)$, is going to be small, as illustrated by the red line. Conversely, when the temperature is decreased, the value of the slope increases (blue line), and pressure decreases more slowly with height. In other words, depending on the temperature of the planet, the Barometric law predicts how the pressure changes with height. If you apply this to planet Earth, you may get one slope. And if you apply it to Venus that has a much higher average temperature, then the pressure is going to drop much more slowly with an increase in height. This is kind of a nice and neat example to show how the temperature influences the change in the pressure with height. This will be of importance for planetary probes that are designed to land on other planets, for example. Of course, different planets will also have different values for g, the acceleration due to gravity on that planet, and this will have additional influence on pressure, as given by the exponential function as well.

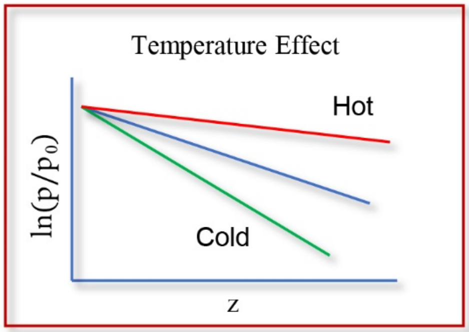

Figure 3.9 Plot of the natural logarithm of the pressure as a function of height at different temperatures, as predicted by the Barometric law. Pressure drops exponentially with height, but the slope of the linear plot depends inversely on temperature.

3.10.5 Effect of molar mass

Since our barometric equation also contains the molar mass in the exponent, the pressure drop depends on this important variable. Notice that since M is in the numerator of the exponent, the pressure drop is exponentially related to the molar mass of the gas. This has a profound effect on the atmospheric composition at different altitudes, in the following manner. So, as the molar mass of a gas increases the numerical value of the exponent increases, pressure drops more rapidly. Thus, as we travel higher and higher, the pressure of heavier gases will fall more quickly than that of a lighter one. This is illustrated in Figure 3.10. The plot of $\ln(p/p_0)$ as a function z shows that the magnitude of the slope of the linear plot (red) for a heavier gas is larger when compared to that of a lighter gas (green line). This has important consequences. If we have a mixture of gases of different molecular weights, then as we travel from the surface of the planet to higher and higher altitudes, the atmosphere will have lesser and lesser proportions of the heavier gases.

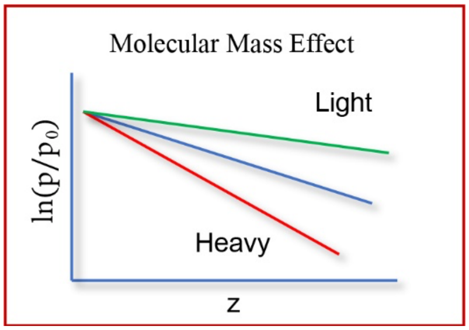

Figure 3.10 Plot of $\ln(p/p_0)$ as a function of height for gases of different molar masses, as predicted by the Barometric law. Pressure drops more quickly for heavier gases (red) than those of lighter (green) gases. Consequently, the atmosphere at higher altitudes will have decreased proportions of heavier gases. Thus, the percent of oxygen in the air at the mountain top is less than at the sea level and decreases exponentially with height. Thus, not only the air pressure is reduced at the mount top, but its composition also changes favoring lighter components of the gas mixture.

This plot predicts the heavier elements will settle down to the bottom and the lighter elements will be at higher altitudes. Thus, the atmospheric composition also changes with height. In our atmosphere, we have nitrogen and oxygen as the two primary components, and therefore, as move to higher altitudes, the composition changes with an increased preponderance of nitrogen when compared to that of oxygen. Thus, not only the atmospheric pressure drops with height, but its composition also changes based on the molecular weights of the gas components present in the atmosphere. This is the reason mountain climbers need oxygen packs to reduce stress due to the lack of oxygen in the atmosphere.

Example 3.10

Calculate the composition of oxygen in the atmosphere at a height of 1 km, if its composition at sea level is 20%, assume 25 ˚C for the average temperature.

$$\ln\frac{p}{p_0} = -\frac{M\,g\,z}{RT} = -\frac{0.032\,kg\;9.8\,m\;\;1000\,m\,s\,s\,K\,mol}{mol\;\;s\,s\,8.31\,kg\,m\,m\,298.15\,K} = -0.1264$$

Or its composition would be 17.5% of oxygen, remaining is nitrogen.

This is the distribution of pressure in a gas column but looking at the term mgz, we recognize that it is the potential energy of the gas particles at the height x. Thus, this is a distribution function of the potential energy of gas particles in the presence of a gravitational field. Replacing the pressure terms in terms of the number of gas particles per unit volume, we write $p = B\,N_z$ and $p_o = B\,N_o$, where B is a constant. The potential energy of the gas particles is given as E_i = mgz.

$$N_i = N_0\,e^{-(E_i/kT)} \qquad \text{Boltzmann distribution of potential energy}$$

Here, N_o is the number of particles in unit volume at the ground level and N_i is the number of particles in unit volume at any height z, where the potential energy (E_i) is given by mgz.

In summary, we show that the pressure decreases exponentially with altitude. Furthermore, this decrease in pressure also depends on the temperature, as well as the molar mass of the gaseous components.

3.11 Molecular Interpretation

The decrease in pressure with an increase in altitude is primarily because of the gravitational field. Since each gas particle has a finite mass, it is subjected to gravity and this attraction due to gravitational field asserts extra pressure at the bottom of the gas column. This is simply because the pressure at any height is due to the weight of the gas column above it (like the hydrostatic pressure of a water column). Thus, the pressure will be the highest at the bottom and drop off as we travel to higher altitudes.

3.12 Applications in daily life

Boyle's law

The expansion of hot gases in the cylinders of the internal combustion engine to produce mechanical work is an example of the application of Boyle's law. While the details of this machine are not important here, expansion of high-pressure gases produces the work needed to move the car. The ignition of a mixture of air and gasoline increases their pressure rapidly, then the pressure of the gas decreases as the volume increases when the piston moves out, moving the car.

Steam turbines provide another example. Nearly 90% of the US electric power is generated using steam turbines, where hot steam at high pressure expands to low-pressure, occupying more volume. In the process, it moves the turbine at high speeds to produce electric power. The same principle is used in jet engines, where hot gases at high pressure expand causing the turbine to rotate and moving the jet plane. Old steam engines of the bygone era also operated on the expansion of high-pressure steam. Thus, one could say that this law is vital to our civilization.

Charles' law

Examples of Charles' law are abundant in daily life. The expansion of air warmed by the sun, at a constant pressure of the atmosphere, is a profound example and this process creates our weather. While details of this phenomenon are not discussed here, air at the surface of the sea is warmed by the sun during the day. This increase in gas temperature (air + moisture) expands its volume as predicted by Charles' law and this warmer moist air is thus less dense, begins to rise into the upper atmosphere. As it reaches the upper atmosphere, it cools, its volume decreases (Charles' law), and condenses into rain, produces our powerful and complex weather system, which can result in dangerous storms.

The pressure law

As the temperature of steam in a boiler increases, its pressure increases and it can then turn the turbines of an electrical generator at a power station, faster. Thus, higher temperatures used in a turbine produce more power than in a steam boiler. The modern jet engines of an airliner run very hot to produce the thrust needed to lift heavy, larger, and larger planes. Similarly, a rapid increase in the temperature of the gases in an internal combustion engine, due to the heat generated by combustion, drives the piston to move a car. Smaller engines are being designed that run at higher temperatures but produce more power, improving the gas mileage. Thus, the temperature dependence of pressure, at constant volume and mass, has a variety of applications in our daily life.

The constant volume thermometer (the turkey thermometer) operates by the increase in gas pressure that is caused during cooking. The pressure inside the turkey increases enough to pop the cap when the temperature reaches a certain value, thus indicating the cooking is complete and the turkey is cooked.

Avogadro's hypothesis

The dramatic increase in food production in the world was achieved due to the Haber process, which produces ammonia from nitrogen and hydrogen according to the proportions discussed. While details of this process are not discussed here, we need to acknowledge that the abundance of food in most countries is due to this one chemical reaction producing a key fertilizer. Needless to mention that this reaction is carried out on a mega scale and reactants are mixed in proportions predicted by Avogadro's hypothesis. This may be the most important chemical reaction created by humankind on this planet.

Ideal gas law

An ideal gas is a concept rather than a real substance. However, it is extremely useful in modeling real gases in physical chemistry. Even though real gases do not exactly obey the ideal gas law, they do approximately follow this law and deviations from the ideal behavior teach us important insights into the nature of gases. Most of the derivations in this book are centered on the concept of the ideal gas, and we will account for deviations of real gases from this ideal behavior when necessary. Thus, all the above examples of empirical gas laws cited in daily life experiences also apply to the ideal gas law.

Dalton's law of partial pressures

Partial pressure is an important concept, and the air is composed of several gases, which normally do not react with each other. Thus, the mole fraction of each component plays an important role in the combustion reactions where the fuel reacts with the oxygen present in the air.

At higher altitudes, the mole fraction of oxygen decreases, which we will show in a later chapter, and athletes often choose to train in Denver, for example, which is about a mile above sea level. At these heights, the mole fraction of oxygen is lower than at sea level, and the body produces additional myoglobin to store enough oxygen in the muscle and hence, such training increases the endurance of the athlete.

The partial pressure of carbon dioxide in our atmosphere is increasing steadily, since the industrial revolution, which is attributed to the burning of fossil fuels. Thus, alternate energy sources that do not produce this greenhouse gas are urgently being sought.

Graham's law of diffusion

Gas purification by diffusion is a major industrial application. Gas separation on an industrial scale is implemented with semipermeable membranes where the lighter gas leaks out more rapidly than the heavier one. This enriches the sample with the heavier gas. Another example is the separation of the uranium isotopes 235 and 238, which differ in their molar masses only by a fraction. Uranium is converted into uranium hexafluoride gas, and the two gas samples are separated by diffusion based on the small differences in their molar masses.

Graham's law is also applicable during the breathing process where the diffusion of oxygen in the lungs is faster than carbon dioxide. Oxygen uptake by blood in the lungs will be faster than the release of carbon dioxide if the concentrations of the two gases are the same in the inbreath. Conversely, smaller toxic gases can be more lethal than larger gas particles.

The Barometric Law

The barometric law has a strong implication in our daily lives. In addition to the effect of a drop in air pressure as we take an elevator ride to a higher floor of a skyscraper, the barometric law is crucial in the design of modern conveniences such as air travel. Some 5000 flights depart daily, in the US alone, and the cabins of the aircraft need to be pressurized for the comfort of the passengers. The weather balloons that are launched daily expand as they reach higher altitudes and finally burst at very high altitudes because the air pressure is too low to contain the gases inside. The low pressure in the upper atmosphere is also responsible ns for the complex weather on the planet as it can promote or inhibit various phase transitions of water causing rain, snow, or drought or cause other weather events.

3.13 Key points developed

Boyle's law

1. Gas expansion at constant mass and temperature results in a decrease of gas pressure, while compression of a gas increases its pressure. Pressure and volume are inversely related.
2. Gases are elastic, and this elastic behavior is exploited in practical applications as struts in a car suspension.
3. As the volume increases at constant mass and temperature, the force exerted by the gas particles is distributed over a larger area, and hence, the pressure (force per unit area) decreases.
4. Boyle's law is widely used in daily applications.

Charles' law

1. As the temperature of the gas is increased, its kinetic energy increases, and the particles move at a higher speed and hence, their momentum is increased which in turn increases the force with which they impact on the walls of the container. Therefore, they exert greater pressure at a higher temperature, but the pressure can be kept constant as we increase the volume appropriately. Thus, volume is proportional to temperature at constant pressure and constant gas mass.
2. An extrapolation of Charles' law to -273.15 ˚C indicates that the gas volume should be zero at this temperature, which is impossible. Thus, this will be the lower limit for the temperature in the universe. At any temperature lower than this, the volume needs to negative which is also impossible.
3. The coefficient of thermal expansion for gas is constant and shared by all gases.
4. The absolute scale of temperature is given as $T/K = (273.15 + t/^\circ C)$.

The pressure law

1. As the temperature of a gas is increased, its kinetic energy increases and the particles move at higher speeds.
2. This increased speed increases the force exerted per unit area, or the gas pressure when the volume and mass are constant.
3. Thus, at constant volume and gas mass, an increase in temperature increases gas pressure and vice versa.

Avogadro's hypothesis

1. Two gas samples at the same temperature, pressure, and volume must contain the same number of particles.
2. One mole is the Avogadro number of particles and characteristic of a chemical substance. Chemical reactions proceed at finite proportions because atoms cannot be split during a chemical reaction, and we need to obey the law of conservation of mass. This is the primary reason we balance chemical reactions. Chemical reactions, in other words, proceed at finite mole numbers of reactants and produce finite mole numbers of products where the total mass is conserved. Each chemical substance has a characteristic mass for the Avogadro number of particles, called the molar mass.

Ideal gas law

1. Ideal gas law $pV = nRT$ is a key equation in physical chemistry and it has been arrived at by combining the empirical gas laws. This is also obtained from the kinetic theory of gases and using the definition of the gas constant, R.
2. Real gases are not ideal, and their behavior deviates to a significant extent under most conditions. The molar mass of a gas sample is proportional to its density.
3. Measurement of gas density as a function of pressure provides a simple method to determine its molar mass.
   $M = \rho RT/p$

Dalton's law of partial pressures

1. As gases are added together at a constant temperature, the kinetic energies of each component gas remain the same, but they are allowed to occupy the entire volume. Thus, the force exerted per unit area by each component is decreased or their partial pressure is less than their initial pressure. As we add more components to the system with their corresponding volumes, the total pressure will be the sum of the pressures exerted by individual components or the sum of their partial pressures.
2. The partial pressure of each of the components in a gas mixture is proportional to their mole fraction.
3. Mole fraction is the ratio of the number of moles of the particular gas component to that of the total number of moles.
4. The partial pressure of a gas in a mixture of gases is the pressure exerted by that component as if it occupies the entire volume by itself

Graham's law of diffusion

1. Diffusion is the rate of gas transport across a unit area in unit time.
2. Effusion is the rate of gas transport through a small opening that is on the order of the average distance traveled between successive collisions between gas particles.
3. Diffusion of effusion rates are inversely related to the square root of the molar mass of the gas.
4. Heavier gases diffuse slower than lighter gases, and this fundamental difference is used in gas separation technologies and may be in gas exchange in the lung.

The Barometric Law

1. Pressure decreases exponentially with altitude.
2. A decrease in pressure with increasing altitude depends on temperature and the molecular weight of the gas.
3. A decrease in pressure with an altitude of a mixture of gases is also accompanied by a change in the mole fraction of the gases unless they all have the same molecular weights.

4. The potential energy of gas particles in a gas column is described by the Boltzmann distribution.

3.14 New terms and units

1. Pressure (p), Volume (V), Temperature (t, ˚C). Pressure has the units of force per unit area and volume has the units of cube of length.
2. pV has the units of (force/length^2)(length^3) = force * length = work. Thus, the unit analysis shows that the constant in Boyle's law has the units of pV.
3. $V = V_o \alpha_o T$, where α_o has units of inverse temperature and volume. Its value for air plays a very important role in our weather systems.
4. Absolute temperature (T), the coefficient of volume expansion (α)
5. Gas mass (W), mole numbers (n)
6. Avogadro's constant (N_A) has units of number per mole. The modern definition of one mole is the number of C atoms in 12.0000 g of carbon isotope 12 and it has the SI unit 'mol'. One mol of a substance contains an Avogadro number of particles (6.02214×10^{23}), as fixed by the 2011 General Conference on Weights and Measures.
7. The units of the constant in the pressure law are given as pressure/temperature (atm/K). Its value plays a very important role in practical applications.
8. Gas constant (R). Although its value is readily obtained by applying the fact that one mol of a gas occupies 22.4 liters at 0 ˚C and 1 atm, we should be able to convert these units into other desired units. Some are given here: https://en.wikipedia.org/wiki/Gas_constant. One useful approximate value is 8.314 J mol^{-1} K^{-1}.
9. Partial pressure (p_i), mole fraction (x_i), total pressure (p_t). Mole fraction is a dimensionless quantity as it is a ratio of two mole numbers. The unit for partial pressure is the same as pressure itself. Given the partial pressure of a component and the total pressure, one can obtain its mole fraction in the mixture.
10. Molar mass (M), Density (ρ). Molecular weight is a dimensionless quantity as it is a ratio of the molecular weight of the sample to that of a reference such as C12. The unit for molar mass, on the other hand, is grams per mole, because it is the mass of one mole of the substance or the mass of Avogadro number of the particles. This is also often expressed in Daltons, where one Dalton is the mass of one mole of hydrogen atoms.
11. Diffusion rate constant has units of moles per second. Height z, acceleration due to gravity g. Units of z are length, and units of g are m/s^2.

3.15 Self Reflection

1. Imagine that you are taking a hot air balloon ride over New Mexico in the early spring. Articulate what gas laws could be applied to explain why the balloon takes off the ground to another passenger who is not a science major.
2. If you are an astronaut scheduled to take off to Mars in a few days, how would you use gas laws to explain to your 5-year-old sibling how the rocket can take off the planet.
3. During the pandemic, there was a severe shortage of oxygen, and you intend to do a startup company to address the issue. Design an apparatus that uses gas laws to separate oxygen from the air at a reasonable cost.
4. Plot pV as a function of temperature at constant temperature and gas mass, and plot 1/p vs 1/V at constant temperature and gas mass.
5. Plot p/v as a function of p for an ideal gas. Explain the attributes of the plot.
6. Plot V/T vs T for an ideal gas. Explain the slope and the X-intercept of the plot.
7. Plot p vs T and p/T vs T for an ideal gas, under these conditions.
8. Plot the number of particles (N) in a gas sample as a function of pressure, at constant volume and temperature. Show the X-intercept value and discuss its implications.
9. Plot pV/nRT as a function of temperature for an ideal gas and carbon dioxide. Comment on your observations.
10. Plot the partial pressure of an ideal gas in a binary mixture (2 components) of ideal gases, as a function of their mole fractions.
11. Plot gas mass as a function of its pressure and find a method to determine its molar mass from this plot.

12. Plot the square of the rate of diffusion of various gases as a function of their molar masses, and comment on what you discover.
13. Certain Himalayan geese survive at high altitudes even at low oxygen levels. Speculate what could be responsible for their successful survival.
14. Since partial pressure of oxygen decreases as we move up the atmosphere, speculate if the partial pressure increases inside a coal mine of 1 km deep.
15. The enzyme nitrogenase is used by certain bacteria to produce ammonia. But these bacteria live in the plant roots of certain legumes where the plant produces leghemoglobin which keeps the partial pressure of oxygen low around these bacterial colonies. Speculate how low oxygen tension maintained around the bacterial colonies.
16. Plot ln (p/p_o) as a function of acceleration due to gravity of different planets of the solar system that have a measurable atmosphere and rationalize why this is the case.

3.16 Further Reading

1. https://ocw.mit.edu/high-school/chemistry/exam-prep/states-of-matter/gases/
2. https://www.youtube.com/watch?v=BhVyiU_dWps
3. https://chem.libretexts.org/Textbook_Maps/Introductory_Chemistry/Book%3A_Introductory_Chemistry_Online!_(Young)/09%3A_The_Gaseous_State/9.2%3A_The_Pressure-Volume_Relationship%3A_Boyle%E2%80%99s_Lawhttps://chem.libretexts.org/Textbook_Maps/General_Chemistry/Map%3A_Chemistry_-_The_Central_Science_(Brown_et_al.)/10%3A_Gases/10.2%3A_Pressure
4. https://en.wikipedia.org/wiki/Barometric_formula

3.17 Self Tests

1. The coefficient of thermal expansion of n moles of an ideal gas of pressure p, volume V is

    a. nR/T

    b. pV/nR

    c. 1/T

    d. nR/p

    e. none of these

2. A mixture of two gases A and B exerts a total pressure of 1 atm. If the mole fraction of A is 0.2, what is the partial pressure exerted by B?

    a. 0.2 atm

    b. 0.8 atm

    c. 0.4 atm

    d. 0.6 atm

    e. none of these

3. The final volume of an ideal gas of 1 atm and 25 liters at 25 °C is compressed to 10 atm is

    a. 2.0 liters

    b. 250 liters

    c. 2.5 liters

    d. 4 liters

    e. none of these

4. The Boyle's Law in terms of pressure 'p', temperature 'T' and volume 'V' is

    a. TV = constant

    b. p/V = T

c. $pV = nRT$

d. $pV/n = RT$

e. none of these

5. The pressure of a gas sample (25 L, 300 K and 500 kPa) upon heating to 500 K at constant volume is

a. 8.33×10^5 Pa

b. 600 Pa

c. 8330 kPa

d. 500 kPa

e. none of these

6. The statement “equal volumes of gases at the same temperature and pressure contain equal numbers of particles” is,

a. Boyle’s Law

b. Charles’ Law

c. Avogadro’s Hypothesis

d. Ideal Gas Law

e. none of these

7. The total pressure of three gases of equal volumes and initial pressures (p) upon mixing is

a. 3(p)

b. p

c. (1/3)(p)

d. p^3

e. none of these

8. The Charles' law for a gas of volume 'V' and temperature 'T' is

a. V is proportional to T

b. V is proportional to 1/T

c. V is proportional to T^2

d. TV = constant

e. none of these

9. Value of t °C on the absolute scale of temperature (Kelvin) is

a. t-273.15

b. t+273.15

c. 273.15

d. t/273.15

e. none of these

10. As the temperature of a gas_, its kinetic energy_____, and the force with which the gas impacts the walls of its container_.

a. increases, increases, increases

b. increases, decreases, increases

c. decreases, increases, increases

d. decreases, decreases, increases

e. none of these

11. The expression for the thermal expansion of a gas is

a. $\left(\frac{\partial \mathrm{V}}{\partial \mathrm{t}}\right)_{\mathrm{p}}$

b. $\left(\frac{\partial \mathrm{V}}{\partial \mathrm{t}}\right)_{\mathrm{T}}$

c. $\left(\frac{\partial \mathrm{V}}{\partial \mathrm{t}}\right)_{\mathrm{p}} dT$

d. $(1/\mathrm{V_o})\left(\frac{\partial \mathrm{V}}{\partial \mathrm{t}}\right)_{\mathrm{p}}$

e. none of these

12. The expression for Charles' law is

a. $\mathrm{V} = \mathrm{V_o}\, \alpha_o (273.15 + \mathrm{t})$
b. $\mathrm{V} = \mathrm{V_o}\, \alpha_o (273.15 + \mathrm{T})$
c. $\mathrm{V} = \mathrm{V_o}\, \alpha_o \mathrm{T}$
d. both a and c

e. none of these

13. The X-intercept of a plot of volume vs temperature (˚C) for a gas has a value of

a. 273.15 ˚C

b. - 273.15 ˚C

c. 0 K

d. 0

e. none of these

14. The expression for the Gay-Lussac law or the pressure law is

a. $\mathrm{p} \propto \mathrm{T}$
b. $\mathrm{p} \propto /1\mathrm{T}$

c. $1/\mathrm{p} \propto \mathrm{T}$

d. $1/\mathrm{p} \propto \mathrm{V}$

e. none of these

15. The ideal gas law is

a. $\mathrm{pV} = \mathrm{nRT}$

b. $\mathrm{pV} = \mathrm{RT}$

c. $\mathrm{pV} = \mathrm{constant}$

d. $\mathrm{p} = \mathrm{nRTV}$

e. none of these

16. The units for the gas constant are

a. atm /K mol

b. atm L^{-1} /K mol

c. atm $^{-1}$ L /K mol

d. atm K L/mol

e. none of these

17. The partial pressure p_I of a gas of mole fraction x_i in a mixture of gases of total pressure p_t is

a. $p_i = x_i / p_t$
b. $p_i = x_i \, p_t$
c. $p_i \, x_i = p_t$
d. $p_i = \, p_t$
e. none of the above

18. The density of the gas (ρ) is related to the molar mass (M), pressure (p), and temperature (T) as

a. $\rho = M/RT$

b. $\rho = pM/RT$

c. $\rho = pM/R$

d. $\rho = p/RT$

e. none of these

19. The rate of diffusion of a gas is

a. directly related to its molar mass

b. inversely related to its molar mass

c. unrelated to the molar mass

d. equal to its molar mass

e. none of these

20. Gases are purified by an industrial process using

a. boiling

b. freezing

c. filtering

d. diffusion

e. none of these

21. What is the pressure exerted by a person weighing ‘W’ kilograms when wearing skates with a total area of cross section 5 cm^2, where g is the acceleration due to gravity?
a. $(Wg/5x10^{-4})$Pa
b. (Wg/5)Pa
c. $Wg/(5x10^{-2})$Pa
d. WgPa/5
e. none of these

22. How is the pressure exerted by a column of fluid of density ‘ρ’ and height ‘h’ on the surface of the moon, with an acceleration due to gravity on the moon of ‘g/5’ expressed?
a. ρgh
b. ρgh/5
c. 5ρgh
d. $\rho g h^2$
e. none of these

23. A plot of pressure versus height is
    a. a decreasing exponential curve
    b. an increasing exponential curve
    c. decreasing linear line
    d. increasing linear line
    e. none of these
24. The proportion of heavy gases to lighter gases in the atmosphere at lower altitudes is_ the proportion at higher altitudes.
    a. higher than
    b. equal to
    c. lower than
    d. can't say
    e. none of these
25. The decrease in pressure with increase in altitude is primarily due to
    a. pressure of the particles
    b. weight of the particles
    c. effect of the gravitational field
    d. composition of particles
    e. none of these
26. In Denver, Colorado (the Mile-High City) the ratio of nitrogen to oxygen in the air is __ that of a city at sea level.
    a. less than
    b. equal to
    c. greater than
    d. can't say
    e. none of these
27. The planet Venus has a much higher average temperature than the planet earth. Therefore, as you gain altitude on Venus the air pressure decreases ___than on earth.
    a. faster
    b. slower
    c. at the same rate
    d. can't say
    e. none of these
28. The logarithm of the pressure with increasing altitude of a gas depends
    a. directly on molecular weight and inversely on temperature
    b. molecular weight and number of moles of gas
    c. directly on the pressure and temperature
    d. electronegativity of the gas, temperature
    e. none of these
29. The pressure in a tall glass column
    a. decreases with gas coefficient of expansion
    b. increases due to the gravity
    c. decreases due to the electronegativity
    d. decreases with height exponentially
    e. none of these
30. The "Barometric Law" is
    a. $p = p_0e^{-(Mgz)}$
    b. $p = p_0e^{-(Mgz/T)}$
    c. $p = p_0e^{-(Mgz/RT)}$
    d. $p = p_0e^{-(Mz/T)}$
    e. none of these
31. The pressure in a tall glass column decreases with height

   a. more rapidly at higher gas temperature
   b. less rapidly at higher gas temperature
   c. the same at all temperatures
   d. can't say
   e. none of these

32. Plot of ln(p/p0) vs height for gas in a tall glass column
   a. decreases exponentially with height
   b. increases exponentially with height
   c. stays the same with height
   d. decreases linearly with height
   e. none of these

33. Pressure in a gas column is
   a. directly proportional to height
   b. inversely proportional to height
   c. decreases exponentially with height
   d. increases exponentially with height
   e. none of these

34. As we go higher in the atmosphere, the composition of the atmosphere will
   a. enrich in heavier elements
   b. enrich in lighter elements
   c. no change in composition
   d. can't say
   e. none of these

35. The cabins of most aircraft are pressurized during a flight because
   a. there is a lack of snacks on the flight
   b. there is a decrease in the humidity
   c. there is a decrease in pressure at high altitudes
   d. it improves the mood
   e. none of the above

3.18 Self Test Key

1. d, 2. b, 3. c, 4. e, 5. a, 6. c, 7. b, 8. a, 9. b, 10. a, 11. d, 12. d, 13. b, 14. a, 15. a, 16. e, 17. b, 18. b, 19. e, 20. D, 21. a, 22. b, 23. a, 24. a, 25. c, 26. c, 27. b, 28. a, 29. d, 30. c, 31. b,32. d, 33. c, 34. b, 35. c.

3.19 Problems

1. A mixture of two gases A and B exerts a total pressure of 1 atm. If the mole fraction of A is 0.2, what is the partial pressure exerted by B? (Ans. 0.8 atm)
2. What is the final volume of an ideal gas of 1 atm and 25 liters at 25 °C when compressed to 10 atm? (Ans. 2.5 L)
3. What is the pressure of a gas sample (25 L, 300 K, and 500 kPa) when heated to 500 K at constant volume? (Ans. 8.33 x10^5 Pa)
4. What is the pressure in bar for a gas sample of 1 mol at standard temperature? (Ans. 101.31 bar)
5. Setup an Excel file and calculate the pressure of an ideal gas of 0.0356 mol at 300 K occupying a volume of 22.1 L in 5 different units of pressure (Hint: Use Table 3.1)
6. During the Covid-19 pandemic there was a global shortage of oxygen and you wanted to start make a startup company to separate oxygen from nitrogen using a diffusion membrane. However, you need to estimate which of these gases effuses faster and by how much. What are your answers/(Ans. oxygen effuses 0.935 times slower than nitrogen)
7. An unknown gas of volume 1 L weighs 5 g at 300 K and 1 atm, what is its molar mass? (Ans. 123.0 g/mol)
8. How many gas particles are present in a mass of 0.005 kg of a gas of molar mass 123 g/mol? (Ans. 2.44x10^{22})
9. An ideal gas of 2.2 L was heated to 400 K from its standard state, what is its final volume? (Ans.3.22 L)
10. Ammonia gas of 17 g was compressed at room temperature from 5 L to 2.2 L, what will be its final pressure? (Ans. 11.12 atm)
11. What is the pressure exerted by a person weighing ‘W’ kilograms when wearing skates with a total area of cross section 5 cm^2, where g is the acceleration due to gravity? (Ans. Wg/5x10^{-4})Pa
12. Considering that air consists of 80% nitrogen and remaining being oxygen, what would be the air pressure at a height of 1.5 km? (Ans. 0.844 atm)
13. The height of Mount Everest is roughly 8,850 m, increasing each day. If the average temperature of air is taken as 10 ˚C, what would be the ratio of nitrogen to oxygen be at its peak? (Ans. 4.67)
14. Bar-headed geese cross Himalayas at a height of nearly 9 km and near 0 ˚C temperature. Due to the thin air at this altitude their red blood cells bind oxygen better. If this adaptation is all due to higher affinity for oxygen, how much higher the affinity should be when compared to low land-dwelling cousins of this geese? (Ans. ~3.5-fold higher affinity)
15. The atmosphere of the Venus mostly consists of carbon dioxide at a much higher pressure of 93 bar and higher temperature of 740 K than on earth. Consider the temperature is independent of height, and calculate to what percent the pressure drops at a height of 1 km from the surface of the Venus? (Ans.93.2%)
16. A hot air balloon of volume 100 m^3 is maintained at a roughly constant temperature of 50 ˚C as it ascends in the cold Arizona desert air of 15 ˚C, on an early Spring morning. If the balloon is considered to have just warm air, how high can it possibly ascend? (Hint, density of air in the balloon should equal to density of air outside, both change with height, Ans. 8979 m)

Chapter 4. The Maxwell Distribution and Maxwell-Boltzmann Distribution

After completing this chapter, you will be able to:

- Distribution function for the properties of an ensemble of objects or particles.
- Recognize that the properties of individual gas particles in a gas sample vary from particle to particle.
- Synthesize the distribution function for the average velocity and average kinetic energy of the gas particles.
- Analyze how the distribution function of gas velocities depend on the particle mass and temperature.
- Calculate the most probable speed, average speed, average kinetic energy and average maximum speed of gas particles.

Goals

- Examine the distribution of molecular velocities of gas particles
- Relate the distribution functions to specific molecular properties such as mass, momentum, and velocity.
- Analyze the velocity distribution (Maxwell distribution)
- Analyze distribution for the kinetic energy (Maxwell-Boltzmann distribution)
- Examine such distribution functions for a few daily examples

4.1 Why Study this?

In this book, we are interested in investigating how do molecular properties vary from particle to particle, even for a pure sample. We will use distribution functions to describe the molecular properties of a collection of molecules and use these to examine why do chemical reactions occur? This question has a very long path to reach the answer. In later chapters, we will learn that chemical reactions require a certain minimum amount of energy to proceed, called the activation energy. Therefore, only those particles of the reactants that possess sufficient energy will produce the product. Thus, we ask what fraction of the gas particles has sufficient activation energy to give products, or what fraction of particles have a specific amount of energy? Since not all particles have the same energy at any given moment, the calculation of this fraction requires a distribution function that describes how the energy is distributed in the gas sample. Since all energy of an ideal gas is kinetic, a distribution of energies implies a distribution of velocities or speeds. Thus, we are interested in figuring out what is the distribution function for the molecular speeds and what is the distribution function for the kinetic energies of the particles. These distribution functions should be in terms of the molecular properties, so that we can understand how these functions will change as a function of molecular mass or temperature, for example. Thus, a clear understanding of distribution functions and their application along these lines is essential. These insights will then help us predict if a given reaction will take place, and if so, what are the desired best conditions such as temperature or pressure to produce the desired product or rapidly achieve the chemical equilibrium?

4.2 Maxwell Distribution of Molecular Velocities

4.2.1 Heterogeneity in property values for a collection of particles

When we have a collection of particles, as in a gas sample enclosed in a vessel, certain properties of the particles will not be identical for each particle. We ask the simple question, do all molecules of a pure gas travel at the same velocity? If they do, then there is no reason for us to go any further. But experiments reveal that not all gas particles travel at the same velocity as the value differs widely from particle to particle. There is usually a distribution of velocities centered around a value. The continuous collisions that occur among the gas particles will result in the exchange of momentum and this will change the speeds and directions of their travel, continuously. Thus, it will be impossible to imagine that all particles will have the same speed.

This situation can be addressed by relating the above problem with that of our daily experiences. We ask, do all the citizens of my town have the same amount of money in their bank accounts? The answer is that it's very unlikely that they all have the same amount but expect that there will be a distribution of amounts among the citizens of the town. Some will have more, and some will have less. We can then ask, how is the wealth distributed among the town citizens? If we know the distribution of the amounts in the bank accounts of all the citizens and then we can design an analysis strategy to estimate the wealth of the town.

The example above shows how the properties of individuals in a collection of objects could be quite different. In physical chemistry, we are interested in knowing how the properties of the individual are related to the collection. The distribution of a given property is analyzed by the corresponding distribution function of the collection, which we will consider soon. Then, we can calculate the average value of that property, the mean, the median as well as the width of the distribution function as well. We will examine each of these properties of distribution functions for our gas sample.

4.3 The velocity distribution

One very important concern of chemists is to control chemical reactions. In later chapters, we will show that the rate of a chemical reaction depends on the thermal energy available for the molecules of the collection in the reaction vessel. In other words, a significant fraction of the molecules should have sufficient energy to overcome the barrier for the chemical reaction (activation energy). Therefore, it would be of interest to ask what fraction of the gas particles have a certain amount of thermal energy and how does this depend on the fundamental properties of the gas particles? The energy distribution function, for example, will answer the above question, as presented later in this chapter. We recognize that the thermal energy of particles will be the kinetic energy, which depends on the speed of the gas particles. Thus, a distribution function for the particle velocity is the starting point and then we can construct the energy distribution function from it.

Now recall that previously we have made an expression for RMS speed as $\sqrt{\frac{3RT}{M}}$ but this value is already averaged over the collection of objects. What we are looking for is an expression that gives us the value for an individual particle and then we construct the distribution function from it. Thus, we are not talking about the root mean square speed, but the exact speed of a given particle. Since we have a collection of particles, we ask what is the probability that a specific particle chosen randomly will have a particular speed, for example, 1 m/s? We will start with the discussion as following:

4.3.1 Infinitesimal velocity interval

Let dn_c be the number of particles present in the infinitesimal velocity interval c and c + dc (Figure 4.1). What does that mean? It means that if I were to pick the velocity interval of c and c+ dc meters per second, then the number of particles that would have their velocities in the interval dc will be dn_c Our assumption is that the velocity interval is so small that the value of dn_c will also be an infinitesimal interval of the number of particles. This kind of analysis is for setting up the distribution function to be integrated. If these intervals are not infinitesimal, then we can't use integral calculus. Thus, our arguments are chosen specifically so that we can use calculus to solve the questions we are asking.

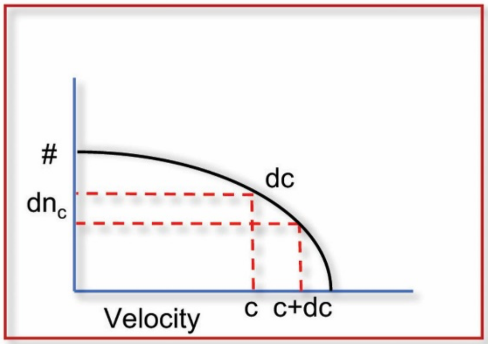

Figure 4.1 Fictitious distribution function for the velocity of a gas sample as a function of the number of particles on the Y-axis *vs* velocities of the particles on the X-axis. Note that the velocity interval c and c + dc is on the X-axis, and the corresponding interval for the number of particles, dn_c is on the Y-axis. The lowest X-value is not zero in this graph but starts at some high value.

4.3.2 Fraction of molecules in velocity interval dc

The fraction of molecules in this velocity interval can be written because we know the number of particles in this small interval (dn_c) and the total number of particles (N) in our sample. So, dn_c divided by N or the fraction $\frac{dn_c}{N}$ is what we will focus on because it is a measure of the particles of our interest. Note that the width of the velocity interval is dc and this is the fraction of molecules present in the velocity interval c and c + dc.

4.3.3 Fraction of molecules present in the interval of unit width

For most practical applications, we ask what is the fraction of molecules in the interval c and c+1 m/s, unit width of velocity. This is obtained by dividing the fraction $\frac{dn_c}{N}$ with the infinitesimal velocity interval dc to give $\frac{dn_c}{Ndc}$. How does this work? The value changes from infinitesimal width to unit width because we are dividing with the infinitesimal width. For example, if five pencils cost one dollar then each pencil costs 1/5 of a dollar. Thus, we are doing very simple algebra to get this new fraction. This is the fraction of molecules present in a unit width of the velocity interval.

4.4 Some examples of common distribution functions

Let us imagine that we go to the grocery store and see a bunch of tomatoes on the shelf with a specific price per pound, irrespective of the individual tomato you choose because the price is per pound. Thus, the price you pay will be proportionally adjusted if you buy a small tomato or a larger one. However, we can get curious and ask how likely is that all the tomatoes on this shelf have the same weight? We weigh the individual tomatoes and plot how many tomatoes have a certain mass, and we will likely obtain a distribution function (Figure 4.2). If we integrate the function over the entire mass range, we will get the total mass of all tomatoes.

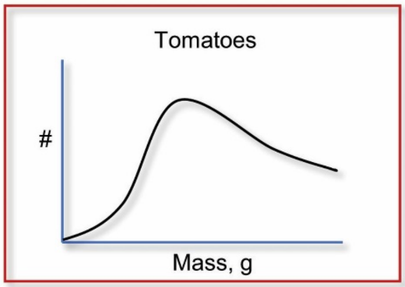

Figure 4.2 Distribution of the mass of tomatoes in a collection at a nearby grocer. If the grocer did not sort them out by size, then one can expect a wide distribution, as shown here. On the other hand, if the grocer sorted out the small ones, medium ones, and large ones into different collections then each of the distributions of these collections will be much sharper. That is, the width of the distribution function tells us how heterogeneous our collection is.

If the grocer did not sort the tomatoes, then there will be very few that will have very low mass and there will be very few with very high mass, and the rest of them will have masses in between. If this distribution is very broad it means the grocer has not sorted them out in terms of size. Since they are being sold by weight, it does not matter. But if they are sold per individual then it is an entirely different story. For example, avocados at my store are sold by number and not by mass, and hence the above analysis becomes very important for the consumer. So, you can see now how these kinds of distribution functions are commercially very important, not just in physical chemistry.

4.4.1 Importance of unit width interval

Now we will discuss the unit width of the interval and its importance. For example, the grocer needs to know the number of tomatoes that weigh between x and x + 1 g to set the price per tomato. If the price is too high then people are less likely to buy and if the price is too low then the store will lose money, and so the price has to be right. We just developed the answer for this issue. That is, dn_x/N gives only the fraction of tomatoes that have a mass between x and x + dx, where x represents mass. This value is not very useful, but if we change the interval width to 1 g, that is x and x + 1 g, then it will be easier to price. Price can be fixed based on the fraction of the total number of avocados that will have a mass of x and x + 1 g, as well as the width of the distribution function. These parameters will give the average mass of the tomato and hence its price, as we will see later.

4.4.2 Pricing airline tickets

A similar situation arises for fixing the airline fares, for example. The amount of fuel consumed depends on the total mass of the passengers carried per trip, among other things. Therefore, one needs to know-how are the weights of the passengers distributed in a flight. What fraction of the passengers have a weight in the interval w and w + 1 kg? Thus, one needs to find out the weights of passengers on a typical flight, and then determine the cost of each ticket. The price is not based on the weight of the passengers alone, but the airline must have a good idea of how the weight is distributed among its passengers.

4.4.3 Grades in a class

Let's take a couple more examples to further dwell on the nature of distribution functions that we are familiar with. We plot the number of students that received a specific grade on the Y-axis, and the score the student received on the X-axis. If every student in the class got the same score, then our distribution function will be a vertical line (Figure 4.3A). The Y-axis has no intercept, and the X-intercept is the grade of any student in the class. This is the sharpest distribution one we can get, but often this is not the case in a real class.

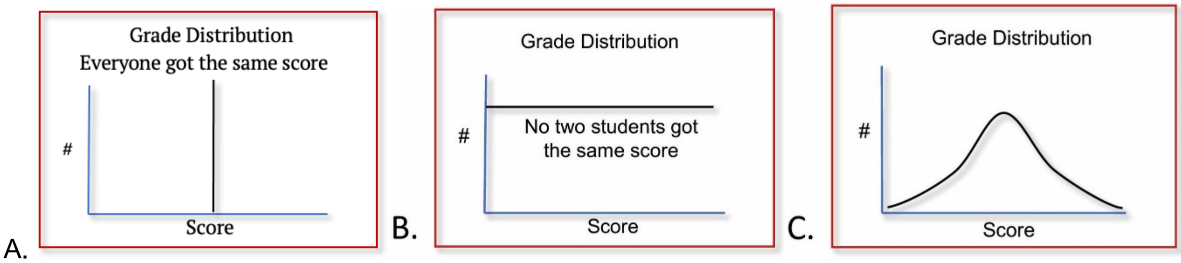

Figure 4.3 A. Grade distributions in a class when all students got the same score. B. Grade distribution in a class when no two students got the same score. C. Plot of grade distribution in a typical class.

Consider a second extreme situation where no two students got the same score, the function will be a parallel line to the X-axis (Figure 4.3B). This is because each assigned grade is unique, and each grade was assigned to just one student. The intercept on the Y-axis is 1 because every student got a different grade and no two of them got the same score. We have only one person associated with each score and the distribution is the widest possible. This is also a very rare possibility in a real class.

We usually have a distribution of scores in a normal class and some students may have gotten the same grade but there will be a distribution. Usually, this looks something like a Gaussian function with a maximum somewhere in the middle and two characteristic minima (Figure 4.3C). There will be very few students who got very low scores, that is the lower limit, and there will be very few students who got very high scores (upper limit) but most of them fit somewhere in the middle. This has a single maximum but occasionally we also see a bimodal distribution.

4.5 The probability distribution functions

The above function in Figure 4.3C is still not in the right form to ask what is the probability that a chosen student will have a score between n and n +1, where n is the score earned. We will do a simple manipulation. We divide the number of students on the Y-axis of any grade with the total number of students in the class. This simple manipulation converts the Y-values into the probability of obtaining that score, and the function is transformed into a probability distribution function. That is let us say that there are a total of 10 tickets in the lottery and you bought one ticket, your probability of winning is 1 over 10. If there are a thousand tickets and you buy all thousand, then you are going to win this lottery for sure. In the same way, the number of students who got a particular score divided by the total number of students (N) gives us the probability of the number of students that would get that score, and this probability distribution function is shown in Figure 4.4.

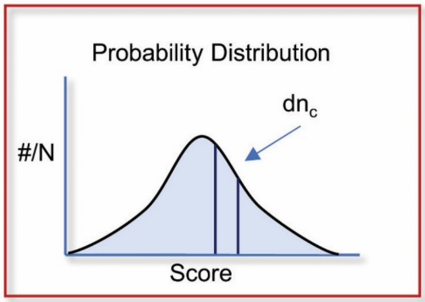

Figure 4.4 Plot of (number of students who got a particular score/total number of students) vs the score. The Y-axis is transformed into probability and the function is now the probability distribution function. The Y-value is also the fraction of students obtaining a particular score, which we already examined earlier.

4.5.1 Probability of scoring between x and x + 1

We are not done yet. We want to know what is the probability that a given student will get a score between x and x+1. If dn_c is the infinitesimal interval on Y-axis then, dn_c/N gives the probability of scoring in the infinitesimal interval, c and c + dc. dn_c is the number of students that got the score within this interval dc. Now if we divide dn_c/N with dc, then we get the probability that a student will get a score between c and c +1, an interval of unit width. For example, the probability of scoring in the range from 80 to 81 percent is now obtained. Thus, we can determine the probability of obtaining any score with an interval of unit width.

4.5.2 Distribution of molecular speeds in a gas

Examine the equation below that is obtained by a detailed derivation from the first principles. The derivation is complex and intricate, and interested students are strongly urged to consult any text, including Castellan. We will take the equation and examine its details and figure out how to apply it to obtain specific properties of gas particles.

$$\frac{dn_c}{N}\frac{1}{dc} = 4\pi(m/2\pi kT)^{3/2}\, c^2\, e^{-(mc^2/2kT)}$$

In the above equation, we have already described the variables before, and you must have recognized that the left side of the equation is the probability per unit width. That is, a given molecule having a velocity of c and c +1 m/s.

The items on the right side are quite familiar to us, except that we recognize k as the Boltzmann constant. One additional comment is that T is the temperature of the sample on the absolute scale. At constant T, for a pure gas of particle mass m, we get a distribution curve, the Maxwell distribution (Figure 4.5).

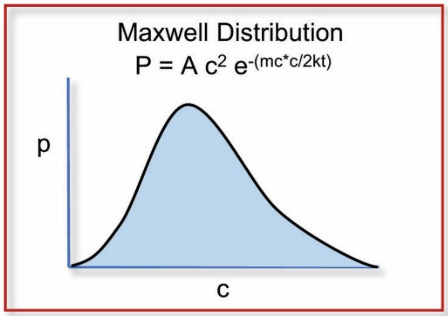

Figure 4.5 Plot of the probability of a particle having velocity in the interval c and c + 1 m/s, as a function of c. The plot has a maximum and two minima. There will be a very small probability that a particle will have a velocity of 0 (left side of the curve). Similarly, there is a very small probability that a particle will have a very high velocity (right side of the curve). But majority of the particles will have a velocity corresponding to the middle of the function.

Here, we have a product of two functions. The first function is c^2 and the y-value increases quadratically with c. The second function is exponential$-mc^2/2KT$. This is decaying exponentially, and these are multiplied to get the probability function. At low c values, the function is quadratic in c, the initial rise of the function will be steep for low values of c, the left part of the distribution function. Under these conditions of low c values, the exponential function of c drops to 1 or close to it. That is e to the power $-mc^2/2kT$ is exponentially decaying.

4.5.3 Limiting values of the function

We recognize that the probability is dependent on the product of two functions of c. For simplicity, write this equation as $P= A\ c^2\ e^{(-mc^2/2kT)}$. Where A is a constant, P is the probability, and the first function is quadratic in c and the second function is the exponential. We also recognize that the exponent has a negative sign, particle mass is in the numerator of the exponent, and temperature T is in the denominator of the exponent.

$$\text{As } c \to 0, \text{ we get } P = A\ c^2 * 1$$

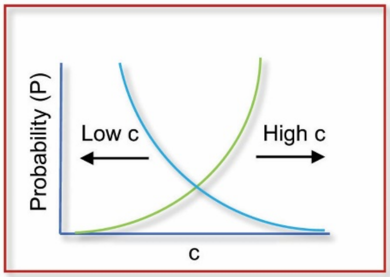

Figure 4.6 The two limiting cases for Maxwell distribution. At low c values, the quadratic function dominates (green curve) while at high c values, the exponential function dominates. In the middle, both functions contribute, and function rises first followed by a decay (blue curve).

We will consider two limiting cases.

1. As we increase the value of c from zero to a certain low value, the function will rise quadratically. The exponential function tends to become zero, because $e^0=1$. So, at low values of c, we should see a quadratic function only (Figure 5.6, green curve).

2. When c goes to high values, the exponentially decaying function supersedes the quadratic function. The value of $mc^2/2kT$ becomes large but due to the negative sign of the exponent, the exponential decays rapidly. Thus, the whole probability function goes to zero even though c^2 is very large because you are multiplying it with the exponential which is close to zero (Figure 4.6, blue curve). As c approaches infinity, we get

$$P=A\ c^2 e^{-(mc^2/2kT)} = 0$$

where the second term goes to zero and hence, probability also goes to zero irrespective of the value of c^2 in the first term.

4.5.4 Effect of particle mass

If you have a heavy mass for the particle, then the function rises quickly, because m is present before the quadratic function. The function also decays fast because m is also present in the exponent of the negative exponential. So, it will both rise fast and decay rapidly (Figure 4.7, black curve) when compared to a lighter gas (Figure 4.7, red curve).

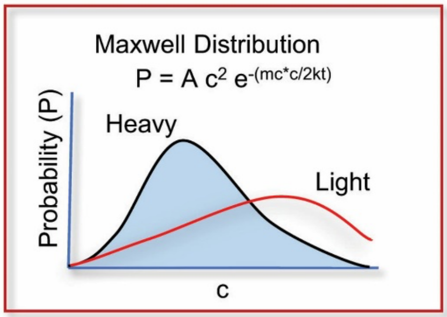

Figure 4.7 Effect of particle mass on the velocity probability distribution function. Heavy particles will have a sharper distribution (black curve) while the lighter gases (red curve) will have a broader distribution. This is due to the occurrence of m at two different locations in the distribution function.

4.5.5 Effect of temperature

Note that temperature also appears at two different locations in the Maxwell distribution. Once before the quadratic function and again in the exponential function. The equation is re-written pulling T-term out using another constant, B.

$$\mathrm{P = B\,(\tfrac{1}{T})^{3/2}\,c^2\,e^{-(mc^2/2kT)}}$$

At low c values, the quadratic function dominates, but it is multiplied by 1/T and hence, as the temperature increases, the rise in the value of the quadratic function is going to be slower and slower (Figure 4.8). At high c values, the exponential function dominates where the temperature occurs in the denominator of the negative exponent of the exponential function, and decay of the function slows down. Therefore, both the rise and the fall of the function are slowed down, the function is stretched out with an increase in temperature.

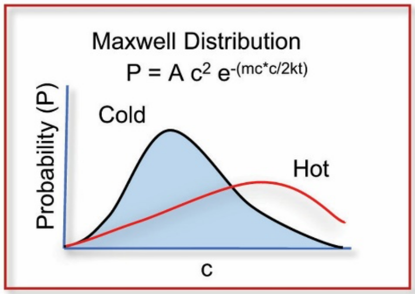

Figure 4.8 Effect of temperature on the velocity probability distribution of a gas sample. At higher temperatures, the probability function is broader with a significant number of particles at higher velocities. There will be a concomitant decrease in the number of particles at lower velocities, and the whole curve shifts to the right and there is a decrease in the maximum.

4.5.6 Most probable speed

It will be important to know the most probable speed for a particle in our collection. This is simply the maximum in the Maxwell distribution function. We can mathematically obtain that value by determining the first derivative of the function and setting it to zero, or the location where the slope of the tangent goes to zero (Figure 4.9A). This is the maximum value shown at the tangent parallel to the X-axis (Figure 4.9A).

$$P = \mathrm{A\,c^2\,e^{-(mc^2/2kT)}\ \text{or}\ \frac{dP}{dc} = A\,2c\,e^{-(mc^2/2kT)} + Ac^2(-\,2mc/2kT)e^{-(mc^2/2kT)}}$$

To obtain the maximum speed, we set this derivative to zero.

$$\mathrm{0 = \frac{dP}{dc} = A\,2c\,e^{-(mc^2/2kT)} + Ac^2(-2mc/2kT)e^{-(mc^2/2kT)}}$$

$$\mathrm{0 = A\,c\,e^{-(mc^2/2kT)}\,[\,2\text{-}\,mc^2/kT]\quad \text{or}\quad (2\text{-}\,mc^2/kT) = 0\quad \text{or}\quad mc^2 = 2kT}$$

The second derivative of the probability function is <0 at this value of c, and it is the most probable speed.

$$\text{most probable speed} = \mathrm{c_{most\ probable}} = \sqrt{\mathrm{2kT/m}} = \sqrt{\mathrm{2RT/M}}$$

This square root dependence shows that the most probable speed will have both a positive and a negative value. In other words, we have a situation where the particle may be moving towards the positive X-axis direction or the negative X-axis direction.

Example 4.1

Calculate the most probable speed of an ideal gas of molar mass 0.016 kg/mol at room temperature.

M = 0.016 kg/mol, T = (25+273) K

$$c_{most\ probable} = \sqrt{2\mathrm{kT/m}} = \sqrt{2\mathrm{RT/M}}$$

$$c_{most\ probable} = \sqrt{2*8.314\ (\mathrm{kg\ m^2\ s^{-2}\ /mol\ K})298\ \mathrm{K}/(0.016\ \mathrm{kg/mol})}$$

$$c_{most\ probable} = \sqrt{2*8.134\ (\mathrm{m^2\ s^{-2}})*298/0.016} = \ 550\ \mathrm{m/s}$$

Note that the average speed will be shown to be larger, next.

We recognize that the most probable speed (c_{mp}) increases as the square root of the temperature and decreases as the square root of the molar mass. Since kinetic energy depends on particle speed and that most probable speed depends on temperature, for a pure gas, temperature and kinetic energy are interrelated. The higher the temperature, the greater the velocity, and therefore the greater the most probable velocity as well (Figure 4.9B). Heavier particles have a lower maximum probable velocity than the lighter particles at the same temperature. Next, we calculate the average speed of gas particles.

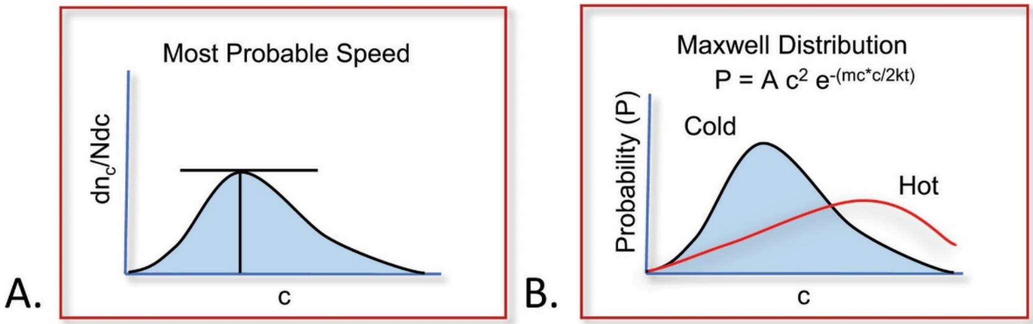

Figure 4.9 A. The most probable speed is obtained by taking the first derivative of the Maxwell distribution function and setting it to zero. B. Increase in temperature increases the most probable speed. For hotter samples, the maximum shifts to a higher c value.

4.5.7 Average speed

This is simply the ratio of the sum of all the values of speed of all particles divided by the total number of particles. To get this, we integrate the distribution function and then divide it with the total number of particles.

$$<c> = (1/N) \int_0^\infty c\ dn_c$$

We previously showed the following and by integrating this with appropriate limits, we will get the average speed.

$$\frac{dn_c}{N} = 4\pi(\mathrm{m}/2\pi\mathrm{kT})^{3/2}\ c^2\ e^{-(\mathrm{mc}^2/2\mathrm{kT})}\ dc$$

We choose the limits 1 to N for the number of particles, and 0 to infinity for the speed of the particles. The integral on the left is the average speed and the value of the integral on the right is then written from a table of integrals.

$$\int_1^N \frac{dn_c}{N} = \int_0^\infty a\ c^2\ e^{-(\mathrm{mc}^2/2\mathrm{kT})} dc$$

$$\text{or} \quad <c> = \sqrt{8\mathrm{kT}/\pi\mathrm{m}}$$

We also recognize that the molar mass of the gas (M) is particle mass (m) multiplied by Avogadro's number and that the gas constant is equal to Boltzmann constant (k) multiplied by the Avogadro's number. So, we replace m/k with R/M.

$$\text{or} \quad <c> = \sqrt{8\mathrm{RT}/\pi\mathrm{M}}$$

So, then all those little intervals from zero to infinity of all the particles from the first particle to the last particle are added and averaged. We recognize that the average speed is related directly to the square root of temperature and inversely related to the square root of the molar mass. This pattern is like the most probable speed, but the numerical values are different. Thus, we discovered, root mean speed, the most probable speed, and average speed. They're all different entities and we need to be able to keep track of their differences. The distribution functions are thus, useful to obtain several different properties of the collection and generally applicable to several common problems in science and daily life.

Example 4.2

Calculate the average speed (<c>) of an ideal gas of molar mass 0.016 kg/mol at room temperature.

M = 0.016 kg/mol, T = (25+273) K

$$<c> = \sqrt{8kT/\pi m} = \sqrt{8RT/\pi M}$$

$$<c> \ = \sqrt{8{*}8.314\ (\mathrm{kg\ m^2\ s^{-2}\ /mol\ K})298\ \mathrm{K}/\pi(0.016\ \mathrm{kg/mol})}$$

$$<c> \ = \sqrt{8{*}8.134\ (\mathrm{m^2\ s^{-2}}){*}298/\pi\ {*}0.016} = \ 621\ \mathrm{m/s}$$

As we see from the previous example, the most probably speed is less than the average speed. The average speed is √(4/π) times larger.

Since the average and most probable speeds depend on the square root of molar mass, isotopes can be separated by this difference. Since chemical reactivities depend on the molecular speeds, the isotopes are expected to react at different rates, another method to separate them.

Example 4.3

How much greater is the average speed of an H_2 molecule than its heavier isotope D_2?

M(hydrogen) = 0.002 kg/mol; M(deuterium) = 0.004 kg/mol

$$\frac{< c >_{hydrogen}}{< c >_{deuterium}} = \sqrt{\frac{8RT}{\pi M_{hydrogen}}\ \frac{\pi M_{dueterium}}{8RT}} = \sqrt{\frac{M_{dueterium}}{M_{hydrogen}}} = \sqrt{\frac{4}{2}} = \sqrt{2}$$

Thus, hydrogen molecules travel slightly faster than deuterium molecules and this difference is used to separate the isotopes by a variety of methods.

4.5.8 Experimental determination of the velocity distribution

Many phenomena could not be explained without the idea of the distribution of velocities of a gas sample, but it took nearly a century to verify and accept it. The apparatus used to measure the velocity distribution is an ingenious one. Gas particles are allowed to escape through a pinhole in a container. The molecular stream is then collimated with a set of slits as if it is a beam of light. Then the collimated beam is allowed to pass through a pair of cogwheels separated by a suitable distance. The molecules that pass through a pair of cogs in both wheels are detected by a sensitive molecular detector. When the cogwheels are rotated at a fixed velocity, only those molecules that can travel from one cog to the next in the given time interval can make it to the detector. Thus, by rotating the cogwheels at different speeds, molecules traveling at different velocities have been quantified. The experiment is similar to that of the measurement of the velocity of light, that you have studied in Physics. The experimental data of molecular velocities supported the predicted velocity distribution function for a given gas sample, confirming the validity of the Maxwells distribution function! Another triumph for the kinetic theory of gases.

4.6 Energy Distribution

Since velocities of gas particles are distributed, so will be their kinetic energies. These are the fundamentals advanced by the kinetic theory of gases. These distribution functions formed a solid molecular basis for chemistry and kinetic theory is considered as a bridge between the down-to-earth thermodynamics and elusive quantum mechanics. Thus, we will continue our journey into the distribution functions.

4.6.1 Maxwell-Boltzmann Distribution

We are concerned with the energy distribution because chemical reactions require a certain amount of activation energy to proceed. We replace the velocity term in the Maxwell distribution with the energy term. Let ε be the kinetic energy of the gas particle and because there is a distribution of speeds, there will also be a distribution of kinetic energy. Since the kinetic energy of gas particles is given by 1/2 mc^2, we can write Maxwell distribution in terms of energy distribution, and that is the Maxwell-Boltzmann distribution of kinetic energy of a gas sample.

We replace dn_c with the infinitesimal interval of the number of particles dn_ε that have certain energy between ε and dε , and write c in terms of kinetic energy.

$$\frac{dn_c}{N} = 4\,\pi\,(m/2\pi kT)^{3/2}\,c^2\,e^{-(mc^2/2kT)}dc$$

$\varepsilon = \frac{1}{2}mc^2$ and $d\varepsilon = (1/2)m\,2c\,dc$ or $dc = (1/mc)\,d\varepsilon = (1/m\sqrt{(2\varepsilon m)})\,d\varepsilon$. By substitution of these into Maxwell distribution we get the Maxwell's energy distribution.

$$\frac{dn_\varepsilon}{N} = 4\,\pi\,(m/2\pi kT)^{3/2}\,(2\varepsilon/m)\,e^{-\frac{\varepsilon}{kT}}\,[1/(m\sqrt{(2\varepsilon m)})]\;d\varepsilon$$

$$\frac{1}{N}\frac{dn_\varepsilon}{d\varepsilon} = 2\,\pi\,(1/\pi kT)^{3/2}\;\varepsilon^{1/2}\;e^{-\varepsilon/kT}$$

In the same manner as Maxwell distribution, we can calculate average energy, most probably energy and root mean squared energy of the gas particles. The average energy is given as follows.

$$<\varepsilon> = \left(\frac{3}{2}\right)nRT$$

Previously, we have seen the total KE as (3/2) nRT and consistent with this expression, where the energy is proportional to the number of moles of the gas under consideration. Note that this value is different from one calculated from average speed, and this is due to averaging before squaring c vs after squaring.

Example 4.4

Calculate the average molar energy of an ideal gas of molar mass 0.016 kg/mol at room temperature.

M = 0.016 kg/mol, T = (25+273) K

$$<\varepsilon> = (3/2)\,nRT$$

$$<\varepsilon> = 1.5 * 1\text{ mol} * 8.314\,(\text{kg m}^2\,\text{s}^{-2}\,/\text{mol K})298\text{ K}$$

$$<\varepsilon> = 3716\text{ kg m}^2\,\text{s}^{-2} = 3.72\text{ kJ}$$

Previously we examined the distribution of potential energy of gas particles in the presence of a gravitational field. This is the Boltzmann distribution of potential energies of the gas particles given as, where E_i = mgz.

$$N_i = N_0\,e^{-(E_i/kT)} \qquad \text{Boltzmann distribution}$$

Here, N_o is the number of particles in unit volume at the ground level and N_i is the number of particles in unit volume at any height z, where the potential energy (E_i) is given by mgz. Now, we will combine the velocity distribution of Maxwell with the potential energy distribution of Boltzmann to get the total energy distribution. This is aptly referred to as the Maxwell-Boltzmann distribution and is given below.

$$\frac{dN_0}{N_0} = 4\,\pi\,(m/2\pi kT)^{3/2}\,c^2\,e^{-\frac{mc^2}{2kT}-\frac{mgz}{kT})}dc$$

Here, N_0 is the number of particles in unit volume at the ground most energy level with energy E_o, and dN_o is the infinitesimal interval of molecules in the total energy interval.

4.7 Molecular Interpretation

Velocity Distribution

Most gas particles travel at different speeds, even at the same temperature, concentration, and pressure of a pure sample of gas. Thus, if we sample different particles, we will measure different speeds and only occasionally two particles will have the same speed, but this probability is readily calculated from the Maxwell equation. This distribution is essentially due to the elastic, continuous collisions between the particles that result in the exchange of momentum. Thus, at any given time few molecules travel at very high velocities and thus, can drive chemical reactions with significant barriers. In a gas mixture, heavier particles are traveling slower than lighter ones. Because the particles are constantly colliding and traveling, a given particle's speed is constantly changing. We also found that the average speed, for example, depends on molecular characteristics such as temperature and mass of the gas particles.

Energy Distribution

Early on, you may have learned that chemical reactions occur because the total Gibbs free energy of products is less than the total Gibbs free energy of the reactants or in simple terms, the products are more stable than reactants. Then, you must have learned that only those reactant molecules that have sufficient energy of activation will be converted to products or that there is the characteristic minimum energy needed for the reactants to become products. Now, we recognize that only a fraction of the reactant molecules will have the necessary energy to become products and that number of reactant molecules with the activation energy depends on the energy distribution. This distribution is given by the Maxwell-Boltzmann distribution. From the distribution function, we can calculate the fraction of molecules that have sufficient energy to become product molecules. Since the gas particles are continuously exchanging energy among them, there will be another set of molecules that have enough energy to react, next and so on. This continues until the chemical equilibrium is achieved or all the reactant molecules are converted to the product molecules. This latter situation is controlled by Gibbs free energy of the reaction, which we will discuss in future chapters.

4.8 Applications in daily life

The Maxwell distribution is used in several industrial applications where the gas particles are separated, purified, liquefied, or reacted with particular substances. When the gasoline is ignited inside the chambers of your car engine, the temperature suddenly rises to very high values. With an increase in temperature, the velocities of the particles also increase, and this increased particle momentum transfers to the piston head and moves the car. Any such scenarios of combustion are good examples.

Every chemical reaction and every biochemical reaction that we encounter is dictated by the energy distribution. This is central to physical chemistry and chemistry in general. Not only chemical processes but even physical processes might have activation energy, such as the dissolution of a solid in a liquid. In all such cases, Boltzmann distribution plays an important role.

Consider that a stream empties into a lake and then the lake overflows into a river. The water from the stream may not have sufficient energy to flow into the river until the lake fills up, which increases the potential energy of the water in the lake until it overflows its banks into the river. Thus, certain activation energy is required for the overflow. However, water molecules do not have a distribution of their potential energies over the barrier, and this is where the analogy stops. But now, consider the evaporation of water. At any temperature, a certain fraction of water molecules will have enough energy to escape into the atmosphere, and the temperature need not be at the boiling point. This is because there is a distribution of kinetic energies in the liquid state and a significant fraction of them will have enough energy to escape into the air, and the lake can dry out over some time.

Energy distribution plays a very important role in biology where the growth depends on the temperature of the biological system. With excessively low temperature, growth is arrested; and growth is optimum in certain temperature ranges. We witness this during every spring in North America when plants begin to grow again after the winter dormancy. At excessively high temperatures, growth is arrested due to the loss in the activities of key biological molecules required for growth, often due to their denaturation or heat damage. These latter processes also require certain activation energy to proceed and hence, controlled by another distribution function. Thus, energy distribution plays an important role in our daily lives at many levels.

4.9 Key points

1. All gas particles do not necessarily travel at the same speed.
2. There is a distribution of speeds of gas particles.
3. The speed of an individual particle is constantly varying with time.
4. The average speed of a gas sample depends on the √temperature and √1/molar mass.
5. Heavier particles travel slower than lighter particles.
6. The average speed at a higher temperature is greater than at a lower temperature.
7. The kinetic energies of gas particles are distributed over a range of values and most of them do not have the same value as another particle.
8. The energy distribution is similar to the speed distribution and the two distribution functions differ in their details but similar in a qualitative manner.
9. The most probable energy, average energy, and the fraction of particles that have finite energy can be calculated from the energy distribution function.
10. The energy distribution is an important concept in evaluating the rates of chemical reactions which will be addressed in later chapters.
11. The total energy of gas particles in a gas column is described by the Maxwell-Boltzmann distribution.

4.10 New terms and units

Distribution functions, probability, average speed, most probable speed, velocity distribution, average energy, most probable energy, probability that a given particle will have a specific energy, and energy distribution. The probability is unitless, and other quantities we have already discussed in previous chapters.

4.11 Self reflection

Based on the material presented here, address the following challenges.

1. Given the space of your classroom, think of 2 different distribution functions that you can construct by polling your classmates.
2. What would be the distribution function for the weight of 0.5 gallon milk cartons from a specific vendor?
3. Do you expect the distribution function for the heights of passengers of a subway car during the rush hour in a large city to be quite different from that of passengers in cars on a highway? Explain.
4. How does the distribution function of student heights in your class compares with that of your university's men's basketball sports team?
5. Plot an anticipated distribution of the weights of tomatoes that are harvested freshly from a farm.
6. Plot the kinetic energies of gas particles as a function of the number of particles with specific energy at a temperature below the critical temperature of the gas and above the critical temperature of the gas.
7. Plot the distribution of kinetic energies of a heavy gas and compare it with that of lighter gas.

4.12 Further reading

1. https://cosmolearning.org/video-lectures/interacting-particles-iii-van-der-waals-equation/
2. https://ocw.mit.edu/courses/chemistry/5-112-principles-of-chemical-science-fall-2005/video-lectures/lecture-14-distribution-molecular-energies/
3. https://ocw.mit.edu/courses/mechanical-engineering/2-57-nano-to-macro-transport-processes-spring-2012/video-lectures/lecture-15-particle-description-liouville-boltzmann-equations/

4.13 Self Tests

1. At higher temperatures, the width of the Maxwell distribution becomes

a. Broader and shorter

b. Sharper and taller

c. No change

d. Taller and sharper

e. none of the above

2. How does the width of the Maxwell distribution for heavier gases differ from that of a lighter gas?
   - a. Broader
   - b. Sharper
   - c. No change
   - d. Taller and sharper
   - e. none of these
3. The ratio of the root mean square velocity to the most probable velocity of a gas is
   - a. $\sqrt{3}$
   - b. 1.5
   - c. $\sqrt{(2/3)}$
   - d. $\sqrt{(3/2)}$
   - e. None of these
4. If a and b are the molecular weights of two gases in a mixture and a>b, then how are the average velocities C_a, C_b of these molecules, respectively, related?
   - a. $C_a = C_b$
   - b. $C_a/C_b = 1$
   - c. $C_a > C_b$
   - d. $C_a < C_b$
   - e. none of these
5. If two gas samples A, and B are at temperatures T_a, T_b and $T_a>T_b$, then C_a, C_b are related as
   - a. $C_a = C_b$
   - b. $C_a/C_b = 1$
   - c. $C_a > C_b$
   - d. $C_a < C_b$
   - e. none of these
6. The average speed of a gas sample depends
   - a. directly on √temperature
   - b. inversely on √molar mass
   - c. both a and b
   - d. gas volume
   - e. none of these
7. The Maxwell distribution of heavy particles is _____ than the lighter particles.
   - a. broader
   - b. sharper
   - c. linear
   - d. steeper exponential
   - e. none of these

8. The average velocity of an ideal gas of molar mass 14 g/mol at room temperature is
   - a. 300 m/s
   - b. 630 m/s
   - c. 400,000 m/s
   - d. 671 m/s
   - e. none of these

9. The standard symbol for absolute temperature is
   - a. v
   - b. V
   - c. C
   - d. T
   - e. none of these

10. In the Maxwell distribution, the quadratic function dominates at ____________ values of c.
   - a. high
   - b. low
   - c. positive
   - d. negative
   - e. none of these

11. In the Maxwell distribution, the exponential function dominates at __________ values of c.
   - a. low
   - b. high
   - c. positive
   - d. negative
   - e. none of these

12. The RMS velocity of an ideal gas is
   - a. $\sqrt{\frac{3nT}{M}}$
   - b. $\sqrt{\frac{3RT}{M}}$
   - c. $\sqrt{\frac{3RT}{nM}}$
   - d. $\sqrt{\frac{3RT}{N}}$
   - e. none of these

13. When everyone in the class scored the same score, the distribution function is
   - a. a line parallel to the axis of the score
   - b. a line parallel to the axis of the number of students
   - c. a curve along and above the axis of the score

d. a curve along the axis of the number of students

e. none of these

14. The probability distribution of the velocity of the gas particles is

a. an exponential function

b. a quadratic function

c. a product of the exponential and quadratic functions

d. a product of rising quadratic and decaying exponential functions

e. none of these

15. The distribution function for the molecular speeds of N gas particles of mass m and velocity c, constant a, is

a. $\frac{dn_c}{N} = (a/T)^{3/2}\ c^2\ e^{-(mc^2/2kT)}$

b. $\frac{dn_c}{N}\frac{1}{dc} = (a/T)^{3/2}\ c^2\ e^{-(c^2/2kT)}$

c. $\frac{dn_c}{N}\frac{1}{dc} = (a/T)^{3/2}\ c^2\ e^{-(mc^2/2kT)}$

d. both b and c

e. none of these

16. The Maxwell distribution is such that as the velocity approaches zero, the probability of a particle with that velocity

a. approaches 1

b. approaches 0

c. approaches infinity

d. independent of c

e. none of these

17. The Maxwell distribution is such that as the velocity approaches infinity, the probability of a particle with that velocity

a. approaches 1

b. approaches 0

c. approaches infinity

d. independent of c

e. none of these

18. The Maxwell distribution is such that as the particle mass approaches zero, the probability of a particle with that velocity

a. approaches 1

b. approaches 0

c. approaches infinity

d. independent of c

e. none of these

19. The Maxwell distribution is such that as the particle mass approaches infinity, the width of the velocity distribution function

a. approaches 1

b. approaches 0

c. approaches infinity

d. independent of c

e. none of these

20. The Maxwell distribution is such that as the temperatures approaches infinity, the width of the distribution function

a. approaches 1

b. approaches 0

c. approaches infinity

d. independent of c

e. none of these

21. The average velocity of a gas particle of molar mass M, velocity c, and temperature T, deduced from the Maxwell distribution is

a. $<c> = \sqrt{(RT/\pi M}$

b. $<c> = \sqrt{(8RT/M}$

c. $<c> = \sqrt{(8RT/nM}$

d. $<c> = \sqrt{(8RT/\pi M}$

e. none of these

22. The most probable speed of a gas particle of molar mass M at temperature T is

a. $\sqrt{2kT/M}$
b. $\sqrt{8RT/M}$
c. $\sqrt{8kT/M}$
d. $\sqrt{2RT/M}$
e. none of these

23. The infinitesimal change in velocity of a gas particle (dc) is related to the infinitesimal change in its kinetic energy (dε) as

a. $dc = m\ d\varepsilon$

b. $dc = (2\ /m)\ d\varepsilon$

c. $dc = \ m\ d\varepsilon$

d. $dc = 2\ m\ d\varepsilon$

e. none of these

24. The number of particles (N_i) with energy ε_i is related to the number of particles in the ground state (N_o) as

a. $N_i = N_i\, e^{-(\varepsilon_i/kT)}$

b. $N_o = N_0\, e^{-(\varepsilon_i/kT)}$

c. $N_i = N_0\, e^{-(\varepsilon_i/kT)}$

d. $N_i = kN_0\, e^{-(\varepsilon_i/kT)}$

e. none of these

25. According to the Boltzmann distribution, the number of particles with infinite energy is

a. infinity

b. zero

c. 1

d. -1

e. none of these

4.14 Self Tests Key

1. a, 2. b, 3. d, 4. d, 5. c, 6. c, 7. b, 8. d, 9. d, 10. b, 11. b, 12. b, 13. b, 14. d, 15. c, 16. b, 17. b, 18. b, 19. b, 20. c, 21. d, 22. d, 23. d, 24. c, 25. b

4.15 Problems

1. What is the ratio of the root mean square velocity to the most probable velocity of an ideal gas? (Ans. √3)
2. What is the average velocity of an ideal gas of molar mass 14 g/mol at room temperature? (Ans. 671 m/s)
3. The weight (kg) of tomatoes in a basket at the store was found to follow the distribution function

$$\frac{dn_x}{N} = (4/\sqrt{\pi})a^{3/2}\, x^2\, e^{-(ax^2)}\, dx$$

4. where x is the weight of one tomato and N is the total number of tomatoes in the basket (very large). If they are being sold at 1$/kg, what would be the average cost of a tomato? (Ans. 2 √(1/πa)$)
5. In the above problem, what is the most probable price of a tomato? (Ans. √a $)
6. In a class of 100 students graded over a range of 1 to 100 (rounded to the nearest whole number), each student received a unique grade. No two students got the same grade. What is the class average? (Ans. 50.5)
7. Design an experiment to measure Boltzmann constant using the gas laws.
8. Design an experiment to verify the distribution of velocities in a gas sample.

Chapter 5. Van der Waals Equation

After completing this chapter, you will be able to:

- Recognize that real gases do not behave ideally, under most conditions.
- Examine the reasons for the deviation from the ideal behavior
- Recognize that the intermolecular interactions are to be accounted for correcting the observed pressure.
- Develop a correction term for the measured volume by accounting for the finite volume of real gas molecules.
- Synthesize the van der Waals equation for gases and apply it for real life examples.

Goals

- Examine the properties of real gases in terms of their departure from ideal gas behavior. Work out the molecular scale details that contribute to these deviations.
- Construct reasonable mathematical corrections to these deviations and arrive at the famous van der Waals equation.
- Write an equation of state for real gases as an extension of the ideal gas equation, using standard physical chemistry approaches.

5.1 Why study this?

Real gases do not behave ideally but we deal with real gases in chemistry. We also deal with real gases for day-to-day applications and industrial applications. Thus, the study of real gases is critical if we were to use our methodology to understand real systems, not just the ideal systems. However, ideal gas lays the foundation to discuss real gases and we will build on the ideal gas model by introducing concrete corrections from experimental observations. For example, real gases can be condensed to liquids under specific conditions, and then they may even be converted to solids. Thus, some of the assumptions that we made under the kinetic theory gases are not valid and appropriate corrections need to be introduced to the ideal gas law for its application to real gases. Thus, these discussions lead to molecular level corrections to the ideal gas law, and these insights are important to understand the nature of the gaseous state. Therefore, this chapter is important in our understanding of the core principles of chemistry.

5.2 Real Gases

By examining the assumptions made in constructing the ideal gas model, we can recognize that real gas behavior would deviate from that of the ideal gas. For example, daily experiences show that real gases can be cooled to condense into a liquid and then eventually to a solid form, under specific conditions. This condensation of the gas to the corresponding liquid or solid phases is possible only if the intermolecular interactions between the gas molecules are not negligible, and these interactions hold the gas particles together in the condensed phases. Real gases must have attractive interactions among the particles. Thus, the presence of intermolecular interactions between the particles of the gas is contrary to the assumption we made in constructing the ideal gas model.

Another important consideration for real gases is their non-negligible molar volume. Since liquids and solids have finite volumes, our gas particles in the real gases must also have a finite volume, another contradiction to the ‘zero volume’ assumption made earlier for the ideal gas case. Thus, at least two major factors, intermolecular interactions, and non-zero volume form the basis for understanding why real gases might deviate from ideal gas behavior. There could also be other reasons for real gases to deviate from the ideal behavior, but at least we need to consider these two important attributes of real gases in the construction of a real gas equation of state. Experimental evaluation of these deviations is observed by examining the compressibility factor, as described below.

5.2.1 Compressibility factor

We will analyze the ideal gas equation by defining a new term called the compressibility factor (Z). This is the ratio of pV to nRT, and from the ideal gas equation, this should be equal to one. When any of these properties deviate from ideal behavior then its value must deviate from 1. This ratio or the Z value can be

>1 or <1 for a real gas, under the specific set of conditions. Thus, we can summarize these deductions as shown below.

$$Z = pV/nRT = 1 \quad \text{(ideal gas)}$$

$$Z <> 1 \quad \text{(real gas)}$$

Let temperature and volume measurements be made with a real gas of fixed mass, at a finite pressure and then calculate Z from it. If the value of Z turns out to be equal to 1 then we can safely conclude that we have an ideal gas behavior being exhibited by a real gas. On the other hand, if Z is >1 or Z <1, then we know that the ideal gas behavior is not obeyed. Therefore, we can easily distinguish between the real gas and ideal gas, and to continue this investigation, we examine Z as a function of pressure. In this manner, we can learn how the real gas behavior changes over this range of pressures. Such a plot is shown in Figure 5.1 with two separate examples.

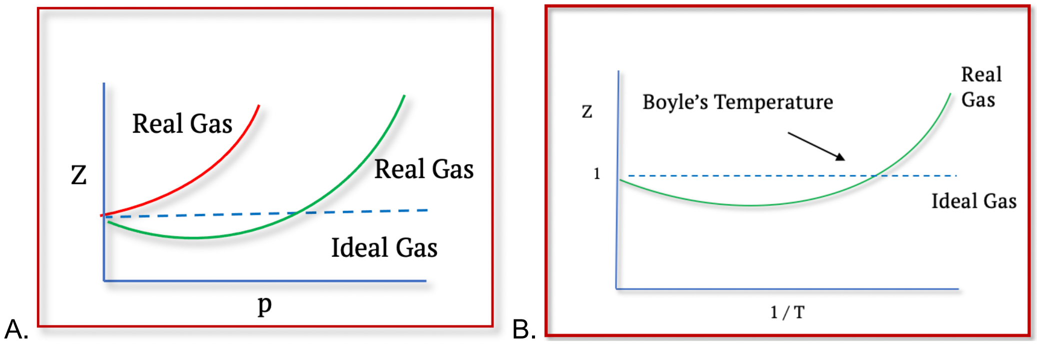

Figure 5.1 A. Plot of the compressibility factor (Z) as a function of pressure (green/red line) for real gases. B. Plot of Z vs 1/T for real gases may indicate a similar behavior (green line) but this line has Z=1 at a specific temperature, Boyle temperature. At this one temperature, the real gas behaves ideally.

The plot of compressibility factor as a function pressure for an ideal gas will be a straight line with an intercept of one (dotted line, Figure 5.1A). At low pressures, the effect of intermolecular interactions will be minor because the gas particles are separated by very large distances. The gas volume far exceeds the volume of the gas particles, at such low pressures. Thus, force and volume corrections will be small and real gases tend to behave like ideal gases (dotted line). Therefore, the compressibility factor will approach 1, even for real gases at such low pressures. The curves for the ideal and real gases meet at Z = 1, in the low-pressure region (Figure 5.1A). So, this is a limiting case where real gases tend to become ideal.

On the other hand, when the pressure of the real gas is significantly high, the intermolecular distances will be shorter and the strength of interactions between the particles will be non-negligible. The total of all the volume of the gas particles is no longer negligible when compared to the container volume. Thus, the real gases deviate from the ideal gas behavior, but the deviations can be either positive or negative (green line) as shown in Figure 5.1A. The positive deviations are indicated when the compressibility factor is greater than 1 (red line). The deviations become larger as pressure increases and real gases deviate from the ideal gas substantially at high pressures.

Example 5.1

The compressibility factor of air at 300 K and 1 bar is 0.9999. What is its molar volume and density, if it contains 80% nitrogen and remaining being oxygen?

Average molar mass of air = molar mass of nitrogen *0.8 + molar mass of oxygen * 0.2

= 28 g/mol *0.8 + 32 g/mol*0.2 = 28.8 g/mol

$$z = \frac{pV}{nRT}; V = \frac{Z\,n\,R\,T}{p} = \frac{0.9999 * 1\,mol * 8.341\,\frac{L\,bar}{K\,mol}\,300\,K}{1\,bar} = 24.94\,\frac{L}{mol}\; or\; density = \frac{28.8\,g/mol}{24.94\,L/mol} = \frac{1.1g}{L}\; or\; 0.0011\,g/mL$$

There are some interesting real gases where Z decreases with pressure first, and then as the pressure increases further, the value of Z begins to rise (green line). The curve crosses the ideal gas line and then increases further with pressure. This is an interesting behavior as the value of Z reaches 1 at some higher pressure. Above or below this pressure, the gas is not ideal but at this pressure, it behaves like an ideal gas. So, we can guess that the correction terms to the ideal gas behavior are of the opposite effect on total pressure and at this pressure, they balance each other out. Thus, different real gases behave in different ways. Only at very low pressures, all gases tend to behave similarly to that of an ideal gas. This is called the low-pressure limit.

Similarly, we can analyze Z as a function of 1/T (Figure 5.1B). Note that this is an inverse plot. At high temperatures, most gases tend to behave like the ideal gas for two reasons. The temperature is so high that the kinetic energy of the gas particles overwhelms the weak intermolecular interactions of the gas particles. Thus, the force correction can be set to zero. The temperature of the gas is so high that the contribution of V to Z is negligible when compared to the contribution of T. Consequently, the volume correction can also be set to zero and at high enough temperatures, real gases tend to behave like ideal gases. We will refer to this as the high temperature limit.

The particular case of the green line shown in Figure 5.1B is of significance. Note that Z at high temperatures is less than one but at low enough temperatures, it is greater than one. As in the case of the Z vs p plot, the green line crosses the blue dashed line (ideal gas behavior) at a certain temperature. At this temperature, other than the high temperature limit, the real gas behavior is identical to that of the ideal gas. This characteristic temperature is called the Boyle temperature. Thus, real gases behave ideally at their corresponding Boyle temperatures, as an exception to the general behavior of the real gases. Before we attempt to modify the ideal gas equation, we will examine the experimental data that laid the foundation for these corrections.

5.2.2 Liquefaction of gases

Laboratory studies show that most of the real gases can be converted to liquids by simply compressing them below a certain temperature called the critical temperature, and this process is the pressure induced liquefaction of gases (Figure 5.2A). By compression, we reduce the volume and increase the pressure. The gas particles are then forced to occupy less and less volume as we compress the gas more and more. If the gas is kept below the critical point (explained later) then the gas particles will eventually begin to condense into a liquid. The liquid is formed when the attractive forces between the particles, the force of attraction increases with a decrease in inter-particle distances, can overcome the thermal energy and form the condensed state. This is how most gases are liquefied industrially and liquefaction of air became a very important step to produce medical oxygen during the pandemic of 2019-2020. Thousands of factories were installed around the world to meet this sudden high demand.

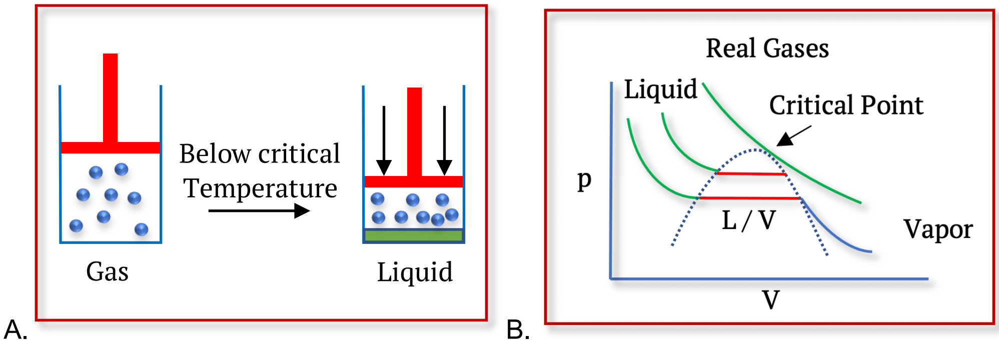

Figure 5.2 A. Liquefaction of real gases by the application of pressure below the critical temperature. B. Plot of Boyle's law at decreasing temperatures for a real gas. Below a certain temperature, the isotherm is distorted and represents three distinct regions, liquid, liquid-vapor mixture, and vapor. The dashed line represents the variation of the liquid-vapor region as the temperature increases.

When we derived the ideal equation, we assumed that the volume of the gas particle is zero when compared to the volume of the container. Now we recognize that this is not the case for real gases. So, we need to make a suitable correction for the molecular volume.

The other is that certain gases are easy to condense, for example, carbon dioxide, which deviates the most from the ideal behavior. Thus, we conclude that the intermolecular forces must be stronger for gases that are easier to condense, and the intermolecular forces contribute to deviations from ideal behavior. Again, we assumed that there are no intermolecular forces between the gas particles of an ideal gas. Thus, there are at least two important considerations for revising the ideal gas model to better describe the real gas behavior.

5.2.3 Critical temperature

As discussed above, real gases can be liquefied by simply applying pressure, below the critical temperature (Tc), and above this temperature, the gas can't be liquefied no matter how much pressure is applied. These observations are described with plots shown in Figure 5.2B.

Plots of pressure versus volume for a given gas, at constant temperature and mass, are the isotherms for a real gas at several different temperatures (Figure 5.2B). Consider the top curve, which is recorded at the highest temperature of all the curves, and each subsequent curve is recorded at decreasing temperatures. Each of these curves has three regions of interest, high-pressure region on the left, the high volume region at the right, and a flat region in the middle. Curve recorded at the highest temperature is a nice smooth curve from high-pressure to low-pressure, Boyle's law plot. Asymptotic variations at high-pressure and high volume are noted.

As we cool the gas below the critical temperature (T_c) and compress it while measuring its pressure, we record the next curve shifted down from the topmost curve, and the shape also changes. The curve is substantially distorted from Boyle's law plot, and a flat region begins to appear. During the flat region, the pressure remains the same, but the volume continues to decrease because of the continuous conversion of the gas into the liquid as we compress the gas. This is the liquid-vapor region. At lower volumes or higher pressures, only the liquid state exists. At higher volumes and lower pressures only the gas phase exists. When all the gas is converted to the liquid phase, the pressure rises very quickly because compressing a liquid is much more difficult than compressing the gas. The plateau region represents the gas-liquid equilibrium state, below the critical temperature. Thus, isotherms of a real gas depend on the temperature of the gas, and below the T_c, they are significantly distorted with three distinct regions appearing in the isotherm. The dashed dome represents the region where the liquid and vapor exist in equilibrium and the maximum point on this line represents the critical state. Above this temperature the gas cannot be liquefied by applying pressure alone. Some value of critical temperature (T_c) and pressure (p_c)are given in Table 5.1.

Table 5.1 Critical temperatures and pressures of a few real gases.

Sample	T_c/K	p_c/atm
He	5.19	2.24
H_2	33.20	12.8
N_2	126.2	33.5
O_2	154.6	49.8
CH_4	190.8	45.8
H_20	647.1	217.7
CO_2	304.2	72.8

5.3 Van der Waals Equation of State

Thus, real gases differ substantially from the ideal gas behavior. An ideal gas can never be liquefied, it has no volume, and it has no intermolecular interactions that are required to form a liquid. And hence, it can never form a liquid or a solid. But the real gases are not like that, as we discussed above. So, we will apply two corrections to the ideal gas equation, the effect of intermolecular interactions and the effect of the finite volume of the gas particles. Van der Waals doctoral thesis describes the first derivations of his equation,[1] which led to winning his Nobel Prize in 1910.[2]

5.3.1 Correction for the intermolecular forces

The formation of the condensed phases by the real gases suggests that there must be attractive interactions between the gas particles. Now, we will consider how these interactions may influence the pressure exerted by the gas particles at the walls of the container. Consider a particle that is in the interior of the container and another that is about to hit the wall of the container. The particle that is present in the interior, sufficiently away from the wall, will have several neighbors. Each of its neighbors will exert attractive forces on the particle of interest (Figure 5.3A). Because this is surrounded by others all around it, the net force exerted on the central particle (red dot) is zero, or negligible. Thus, there will be no net force acting on the particles that are in the interior of the container. Now, consider the particle near the wall of the container which is about to hit the wall and exert pressure (Figure 5.3B). The number of particles surrounding the colliding particle (red) is disproportionately distributed, with more of them behind it than in front of it. Thus, the particle that is about to collide with the wall experiences a net force attraction toward the bulk of the container, and thus lowering the force with which this particle collides with the wall. Thus, the particle will exert less pressure at the container wall than expected when there are no such attractive forces between the particles.

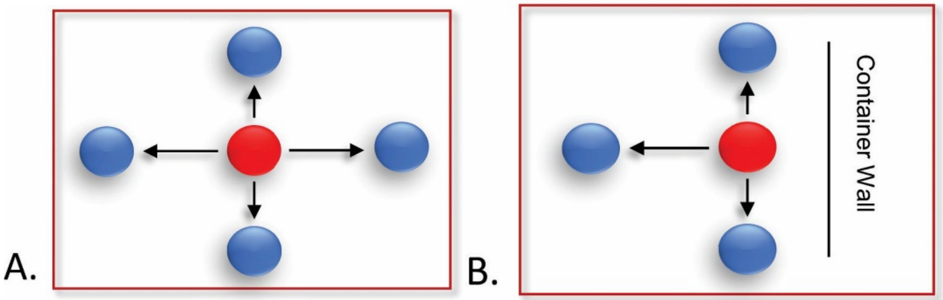

Figure 5.3 Effect of intermolecular forces on the pressure exerted by a real gas (effect of intermolecular interactions). A. The particle in the middle is equally attracted in all directions and has no net force of attraction. B. The particle near the wall surface has more particles on one side than the other and hence, there is a resulting force acting on the particle pulling it away from the wall.

And so, the particles that are about to hit the wall are being pulled back. So, when it collides with the wall it will have less momentum, and it exerts less force on the wall. We can treat this problem mathematically and express the correction in terms of the properties of the gas.

Consider two volume elements of the gas V_1 and V_2 (Figure 5.4). The force of attraction experienced by the gas particles enclosed in V_1 is proportional to the number of particles in V_2. If we double the number of particles in V_2, then the force of attraction exerted by these particles will also double. Therefore, the force is proportional to C_2, the concentration of particles in V_2. In the same manner, the force of attraction between the two volume elements will also double if we double the number of particles in V_1. Therefore, the force of attraction is proportional to C_2 and C_1. Therefore, the force of attraction will be proportional to C_1 multiplied by C_2, but C_1 equals C_2, as the gas is uniformly distributed throughout the container.

Thus, the force of attraction is proportional to the square of the concentration, and the measured pressure will be less than that of the ideal gas. The correction term for pressure should be proportional to $1/\overline{\mathrm{V}}^2$ where $\bar{V}$ is the molar volume. Writing 'a' as the proportionality constant, the correction term is $\mathrm{a}/\overline{\mathrm{V}}^2$. The proportionality constant is called the van der Waals constant, 'a'. Then, we add this correction to the experimentally measured p to obtain the pressure, which will be equivalent to that of an ideal gas. So, $\mathrm{p}+\frac{\mathrm{a}}{\overline{\mathrm{V}}^2}$ is the pressure correction term. However, the value of 'a' depends on the gas sample, and hence the generality of the gas law is lost. That is, each gas will have its equation of state because the value of 'a' depends on the identity of the gas sample.

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[1] van der Waals, J. D. (1873). *Over de Continuiteit van den Gas- en Vloeistoftoestand*. University of Leiden.

[2] "J. D. van der Waals, The equation of state for gases and liquids". *Nobel Lectures, Physics 1901-1921* (PDF). Amsterdam: Elsevier Publishing Company. 1967. pp. 254–265.

The pressure correction term: $(p + \frac{a}{\overline{V}^2})$

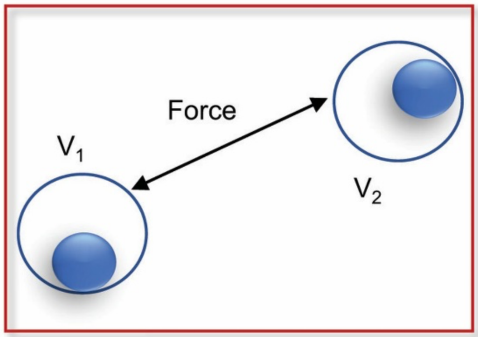

Figure 5.4 Effect of forces of interaction between two volume elements of the gas on gas pressure.

5.3.2 The volume correction

Volume correction is important because the particles of real gases have finite volumes. Each particle occupies a certain volume, and this volume is not available for the remainder of the particles. That is, if we take a big empty container that has a volume V and add the first gas particle, it would occupy a certain volume of the container. As we add the second particle to the container, it doesn't have access to all the volume of the container because some of this volume is already occupied by the first particle. The second particle can only occupy the total volume minus the volume of the first particle. Thus, the third and subsequent particles will have less and less volume to occupy as we load the container with the remaining particles. Thus, we need to correct the actual volume available for the gas particles by taking into consideration the finite volume of the individual gas particles.

Thus, the measured $\overline{V}$ is larger than the $\overline{V}_{ideal}$ and the gas particle accesses less volume than measured in the experiment. Thus, $(\overline{V} - b)$ where 'b' is another van der Waals constant, the volume correction term. It will be appropriate to assume that the value of b will be proportional to the volume of the corresponding liquid or solid.

The volume correction: $(\overline{V} - b)$

5.3.3 The van der Waals equation

These pressure and volume corrections were applied by van der Waals to describe the behavior of real gases, more accurately than the ideal gas equation. But the simplicity of pV = nRT is lost and the equation is specific for each gas in the sense that each gas will have specific values for 'a' and 'b'. Thus, a certain price is to be paid to obtain greater accuracy for the measurements and a better analytical understanding of gas behavior. Substituting these corrections into the ideal gas equation, we obtain the van der Waals equation.

$$(p + \frac{a}{\overline{V}^2})(\overline{V} - b) = RT$$

There's no real need to memorize this equation and we can think about the logic presented here and be able to deduce the correction terms. The constants 'a' and 'b' will have appropriate units, and we encourage you to figure them out. The constant 'a' is a measure of the intermolecular forces, and it is larger for gases that can be liquefied much more readily (Table 5.1). This is because gases that are easy to liquefy would have stronger intermolecular interactions, and the correction should be larger to the pressure term. Along these lines, we would expect that b is a measure of the molecular volume of the real gas. So, those that have larger molar volumes would have greater values for 'b' (Table 5.2).

Table 5.2 Van der Waals constants for a few real gases[3]

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[3] https://en.wikipedia.org/wiki/Van_der_Waals_constants_(data_page)

Sample	a / (atm L^2/ mol^2)	b / (L / mol)
He	0.034	0.024
H_2	0.247	0.0266
N_2	1.37	0.0387
O_2	1.38	0.0317
CH_4	2.29	0.0428
H_2O	5.54	0.0349
CO_2	3.66	0.0427

Under the limiting conditions of the ideal gas, both 'a' and 'b' will vanish and the van der Waals equation reduces to the ideal gas equation. Now, consider the two other limiting conditions under which the real gases approach ideal behavior. One is at very low pressures, and the other is at very high temperatures, and we already discussed how deviations from ideal behavior are negligible, under these conditions.

Example 5.2

What is the pressure exerted by a van der Waals gas of one mole, at 25 ˚C, occupying a volume of 5.0 liters? Assume that the gas is carbon dioxide.

Use the values of ‘a’ and ‘b’ for carbon dioxide in $(p + a/\overline{V}^2)(\overline{V} - b) = RT$ or $p = \left[\frac{RT}{(\overline{V}\text{-}b)}\right] \text{-}a/\overline{V}^2$

T = 25 ˚C = (273+25) K; $\overline{V}$ = 5.0 L/1 mol; R= 0.082 L atm/mol K; a = 3.66 atm L^2 mol^{-2}; and b= 0.428 L/mol^{-1} for CO_2

After substituting these values and solving for p, we get

$$p = \frac{0.082\ L\ atm\ 298\ K\ mol}{mol\ K\ (5.0-0.428)L} - \frac{3.66\ atm\ L^2 mol^2}{mol^2\ 25\ L^2} = \frac{0.082*298\ atm}{(5.0-0.428)} - \frac{3.66\ atm}{25} = 5.198\text{ atm}$$

5.3.4 Van der Waals Isotherms

The van der Waals equation is cubic in molar volume (shown below) and when we solve for $\overline{V}$, for example, we obtain three roots, or three values. This is an unsettling situation because each gas sample has one specific volume, under a specific set of conditions. This situation is resolved by looking at the van der Waals isotherms or the plot of p vs $\overline{V}$ at constant T (Figure 5.5). At temperatures higher than the critical temperature, one expects isotherms with smooth changes in pressure and volume. However, at temperatures below this, the situation changes drastically as explained in Figure 6.2B.

$$\overline{V}^3 - \left(b + \frac{RT}{p}\right)\overline{V}^2 + \frac{a}{b}\,\overline{V} - \frac{ab}{p} = 0$$

As the volume is reduced by compressing the gas sample, the real gas begins to condense into the liquid state. This region is represented by the flat region in the isotherm, shown in Figure 6.5 as well. At much lower volumes, the gas is completely condensed into the liquid state and the compression of the liquid is much harder and the pressure rises very steeply. This entire isotherm is described by a cubic equation where the liquid and the vapor regions are connected by the red dashed line. The horizontal line represents the isobar where there are three possible values for the volume. At the high end of the flat region, one of the roots is the volume of the gas just before the condensation begins. At the low end of the flat region, the volume represents that of the liquid where all the gas is condensed. This is the second root predicted by the van der Waals equation. The third is the mid-point where the red dashed line crosses the isobar, and it is in the liquid-vapor region where both phases coexist.

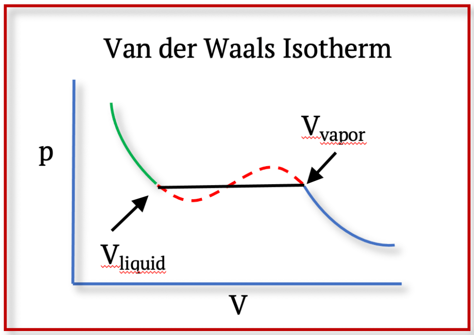

Figure 5.5 Van der Waals isotherms are cubic fits to the experimental isotherms. The red dotted line connects the liquid and vapor isotherms in the cubic fit describing the entire experimental curve.

The entire isotherm is then represented by the above cubic equation where the liquid and vapor phases are connected by the isobar. This equation successfully predicts the conversion of the gas to the liquid phase and provides a mechanism to explain the phase transition. Thus, the van der Waals equation is a big improvement over the ideal gas law applied to real gases. It can successfully describe the experimental data for many gases.

At the Boyle temperature (Tb) the compressibility factor Z=1, and using molar volume of the gas, we can show that $T_b = \frac{a}{Rb}$ where a and b are the van der Waals constants and R is the gas constant. This is not strictly valid for all gases, and deviations are to be expected.

Example 5.3

Using the van der Walls constants given in Table 5.2, compare the Boyle temperatures of water and carbon dioxide.

$$T_{b(water)} = \frac{a_{water}}{Rb_{wqter}} = \frac{5.54\ L^2 atm/mol^2}{0.082\ L\ atm/Kmol * 0.0349\ L/mol} = 1934\ K$$

Similarly, for CO_2 we get a value of 1044 K. These are different from experimental values but close enough for comparison between the two substances. The larger value of water is due to its stronger attractive interactions increasing it's a value over that of b, while the b value of CO_2 is slightly larger than that of water, as expected.

As above, the Tc value of gas is also related to the van der Waals constants, approximately because the deviations are largest at the critical point but given by $T_c = \frac{8\,a}{27\,R\,b}$ where a and b are the van der Waals constants.

Example 5.4

Compare the critical temperatures of water and carbon dioxide obtained from van der Waals equation and with those given in Table 5.1

$$T_{c_{water}} = \frac{8\ a_{water}}{27\ R\ b_{water}} = \frac{8 * 5.54\ L^2 atm/mol^2}{27 * 0.082\ L\ atm/Kmol * 0.0349\ L/mol} = 573\ K$$

Similarly, for CO_2, we get a value of 309 K. The values in Table 6.1 for water is 647 K and that of CO_2 is 304 K, which are in reasonable agreement from the value calculated above. The deviation for water is significantly higher due to stronger intermolecular interactions than CO_2 which has much weaker intermolecular interactions.

5.4 Molecular Interpretation

In chemistry, we talk a lot about van der Waals forces but often focus on the repulsions rather than attractions, as discussed here. This is because the sign and magnitudes of these interactions depend on inter-particle distances. The forces are attractive when this is greater than the van der Waals radius but become repulsive below this radius. In our correction for pressure, we are concerned with interactions at distances longer than this radius of our particle but for volume correction, we are concerned about repulsive interactions below this radius.

The van der Waals interactions arise due to many different molecular and atomic forces, commonly referred to as dispersive forces. These arise due to interactions between particles arising from the unsymmetrical distribution of electrons around the nuclei. This unsymmetrical distribution results in transient dipoles and these transient dipoles are one of the major forces contributing to the dispersive interactions. For example, even in the case of He, the gas can be liquefied, and hence, it has interatomic attractive interactions at some distances. These arise due to transient dipoles and these latter are created by transient unsymmetrical distributions of electrons in the He atom. That is the instance when both electrons are one side of the atom, then there will be an instant dipole created and this can interact with the instant dipoles of other He atoms. Thus, any system that has electrons and nuclei will have transient dipoles and will have significant attractive interactions at certain inter-particle distances. When the particles are brought closer than the van der Waals radius, repulsive interactions kick in and the particles separate, or else the particles should spontaneously condense, which does not happen. Thus, when He atoms collide with each other, for example, they are not stuck together, unless the temperature is close to its boiling point, a few kelvin.

5.5 Applications in daily life

One spectacular example of van der Waals attractions is the Gecko, and it can crawl on ceilings upside down. This is favored by the cushions on its feet that provide very close contact with the ceiling surface. The contact is so close that van der Waals attractive forces are strong enough to hold the critter against gravity. High number of contact points per unit area also helps increase the total strength of these interactions.

Many different types of glue that we use work based on the van der Waals interactions. For example, starch is a good glue for paper. When a starch solution is applied to paper and allowed to dry, it forms a thin film between the two pieces of paper to be glued. Starch may form hydrogen bonds with cellulose because the starch molecules and paper surface are brought close enough to hold the two pieces of paper together via hydrogen bonding and/or simple mechanical interlocking. At these distances, van der Waals interactions further augment the attractive forces to hold the glued objects together. There is no covalent bonding because we can easily separate the glued paper by dissolving the starch in water. Many different non-reactive glues work this way.

5.6 Key points

1. Attractive forces between gas particles reduce the force with which the gas possible particles collide with the container wall. Thus, the force of attraction reduces the experimentally observed pressure. Therefore, a correction needs to be added to the experimentally observed pressure. This correction term depends inversely on the molar volume to the power two because force is inversely related to the square of the distance (fundamental law).
2. The existence of attractive forces among the gas particles is supported by the fact that they can be condensed into liquids or solids where these attractive forces hold the particles together. For example, the heat of vaporization is a measure of these attractive forces in liquids. In a gas, these are much weaker due to their larger distances of separations.
3. Each particle of a real gas occupies a finite volume of the container and hence, other particles cannot have access to that volume. In other words, the measured volume is the sum of the volumes of all the gas particles plus the volume available for the gas to occupy. Thus, a correction term needs to be subtracted from the measured volume to obtain the volume available for the gas to occupy.
4. The finite volume of the gas particles is supported by the fact that they can be condensed to liquids and then on to solids.
5. The simplicity of ideal gas is lost in the van der Waals equation, and it is restricted individual gases with their own a and b constants. It is cumbersome to use but better in explaining experimental data than the ideal gas equation.
6. Van der Waals equation is no longer used widely but its importance is in supporting the kinetic theory of gases and supporting the molecular nature of gases. It also established a revolutionary onset of intermolecular interactions which are very important in modern chemistry.
7. Van der Waals equation also describes the continuity of states from gas to liquid and beyond and defines the critical points of fluids.

8. Van der Waals equation provided the first theoretical justification for critical point and successfully predicted its value for specific gases.
9. It also expanded the gas equation to mixtures of gases, solutes dissolved in solvents, or even polymer composites.

5.7 New Terms and units

Molar volume, van der Waals constants a and b, critical point, liquefaction, and isotherm. Examine the van der Waals equation and deduce the units of the constants, a and b. Check your answers by examining Table 5.1, in this chapter.

5.8 Self Reflection

1. Hypothesize that the forces of attraction in the gas are proportional to the heat of vaporization of the corresponding liquids. Design a plot of experimental data available to test this hypothesis.
2. If van der Waals constant 'b' is proportional to the molecular volume, then test the hypothesis that this is proportional to the molar volume or molar density of the corresponding liquid, using available data.
3. Using the cubic form of the van der Waals equation, can you predict the critical point of a given gas? (hint: at the critical point all three roots of the equation are equal, or only one real root exists).
4. If van der Waals forces can be both attractive, as in pressure correction, or repulsive, as in volume correction, predict how would these forces vary with intermolecular distances. Make a plot of force vs distance where both attractive and repulsive forces are plotted together. Verify your plot by comparing it with the so-called Morse potential.
5. Once upon a time, a Japanese company made a flexible plastic ball that would attach to a wall when thrown at, but would slowly descend the wall on its own, without detaching. Explain on a molecular scale, how this can happen.
6. The company 'Command' makes hooks to hang photos on walls. The hook is attached to the wall with a piece of soft polymer and the hook can be detached easily without damaging the wall. How does that work?

5.9 Further Reading

1. https://ocw.mit.edu/courses/physics/8-422-atomic-and-optical-physics-ii-spring-2013/video-lectures/lecture-10-van-der-waals-and-casimir-interactions/
2. http://www.chemistry2011.org/ResourceFiles/5_60_lecture1.pdf
3. https://cosmolearning.org/video-lectures/interacting-particles-iii-van-der-waals-equation/
4. https://chem.libretexts.org/Textbook_Maps/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical_and_Theoretical_Chemistry)/Physical_Properties_of_Matter/States_of_Matter/Properties_of_Gases/Real_Gases

5.10 Self Tests

1. The correct order of increasing van der Waals constant 'b' is

a. hydrogen, oxygen, chlorine, bromine

b. oxygen, chlorine, bromine, hydrogen

c. bromine, chlorine, oxygen, hydrogen

d. hydrogen, oxygen, bromine, chlorine

e. none of these

2. The temperature at which the distinction between the gas and the liquid vanishes is

a. Boyle temperature

b. Critical temperature

c. Boiling point

d. Sublimation point

3. The gas compressibility factor is
    - a. used to describe ideal gases only
    - b. is the ratio of pV to nRT
    - c. 1 for an ideal gas
    - d. b and c
    - e. none of these
4. The Boyle Temperature is the temperature at which
    - a. any gas behaves ideally
    - b. the compressibility factor is greater than 1
    - c. the compressibility factor is less than 1
5. Attractive forces between gas particles the force with which gas particles collide with the wall of their container.
    - a. increase
    - b. decrease
    - c. do not affect
    - d. can’t say
    - e. none of these
6. van der Waals constant “a” is a measure of:
    - a. molecular volume
    - b. compressibility factor
    - c. intermolecular forces
    - d. molecular weight
    - e. none of these
7. van der Waals constant “b” is a measure of:
    - a. molecular volume
    - b. compressibility factor
    - c. intermolecular forces
    - d. molecular weight
    - e. none of these
8. Units of van der Waals constant “a” are
    - a. L/mol
    - b. L/mol2
    - c. atm*L2
    - d. (atm*L2)/mol2
    - e. none of these
9. Units of van der Waals constant “b” are
    - a. L/mol

b. L/mol2

c. atm*L2

d. (atm*L2)/mol2

e. none of these

10. What is the pressure exerted by one mole of a van der Waals gas (carbon dioxide), of 10 L at 30˚C?

a. 260 atm

b. 3.9 atm

c. 2.6 atm

d. 3.7 atm

e. none of these

11. One major difference between the ideal gas and real gases is

a. the lack of intermolecular forces in real gases

b. the presence of intermolecular forces in gases

c. the higher velocities of particles of real gases

d. poor purity of real gases

e. none of these

12. One major difference between the ideal gas and real gases is

a. the zero volume of each particle of a real gas

b. finite volume of the particles of a real gas

c. the non-zero pressure exerted by real gases even at 0˚C

d. both a and c

e. none of these

13. One reason real gases can be condensed to a liquid or solid is

a. the lack of intermolecular forces

b. the presence of dipoles

c. the finite volume of these particles

d. the presence of intermolecular forces

e. none of these

14. The compressibility factor for an ideal gas is

a. zero

b. one

c. <1

d. infinity

e. none of these

15. The plateau region in the plot of pressure vs volume of a real gas, below the critical temperature, is

a. due to the supercritical phase

b. solid formation

c. condensation to a liquid

d. could be either b or c

e. none of these

16. Above the critical temperature the real gases

a. can’t be solidified

b. can’t be liquefied

c. can’t evaporate

d. both a and b

e. none of these

17. The parameter ‘a’ in the van der Waals equation corrects for

a. molar volume

b. molecular volume

c. intermolecular forces

d. gas temperature

e. none of these

18. The correction for pressure of a real gas in the van der Waals equation is

a. $(p - \frac{a}{\bar{V}^2})$

b. $(p + \frac{a}{\bar{V}^2})$

c. $(p + \frac{a}{\bar{p}^2})$

d. $(p + \frac{a}{\bar{T}^2})$

e. none of these

19. The volume correction term in the van der Waals equation is

a. $(\bar{V} - b)$

b. $(\bar{p} - b)$

c. $(T - b)$

d. $(\bar{n} - b)$

e. none of these

20. The van der Waals forces are

a. only attractive but not repulsive

b. only repulsive but not attractive

c. either attractive or repulsive

d. neither attractive nor repulsive

e. none of these

5.11 Self Tests Key

1. a, 2. b, 3. d, 4. a, 5. b, 6. c, 7. a, 8. d, 9. a, 10. c, 11. b, 12. b, 13. d, 14. b, 15. d, 16. d, 17. c, 18. b, 19. a, 20. c.

5.12 Problems

1. 1.What is the pressure exerted by one mole of a van der Waals gas (carbon dioxide), of 10 L at 30˚C? (Ans 2.6 atm).
2. Compare the pressure estimated from the above with that of the corresponding ideal gas and discuss the significance of the percent deviation.
3. Using the van der Waals constants, calculate the Boyle temperature of water vapor and carbon dioxide. (Ans. 1934 K and 1044 K)
4. Calculate the Critical temperatures of water and carbon dioxide using the van der Waals constants and then explain the deviations from the known values, if there are any. (Ans. 573 K, 309.5 K)
5. Explain how the critical temperature and the Boyle temperature are related via the van der Waals equation and discuss the molecular features of this link between the two temperatures.
6. Explain why real gases behave like an ideal gas at the Boyle temperature.
7. Explain why the deviations from ideal behavior are large around the critical temperature of the gas.
8. State and explain the principle of the continuity of state.
9. The reduced van der Waals equation of state is obtained by dividing the p, V_m and T values with the corresponding values for the gas at its critical temperature. Derive this reduced equation and show that the corresponding compressibility factor is 0.375 for any van der Waals gas.
10. Discuss the properties of supercritical carbon dioxide and its applications.

Chapter 6. Equations of State for Liquids and Solids

After completing this chapter, you will be able to:

- Synthesize the equations of state for liquids and solids, based on experimental parameters.
- Recognize that the equations of states for liquids and solids are similar to each other.
- Develop a model to describe the heat of evaporation of a liquid
- Examine a non-calorimetric method to measure heats of evaporations of liquids.

Goals

- Equations of state for liquids and solids will be developed. Briefly discuss the structure of liquids based on experimental observations.
- Connect the condensed phases with that of their corresponding vapor phase.
- Evaluate the energy changes when liquids evaporate or the heat of evaporation.

6.1 Why Study this?

Most substances that we experience daily are liquids and solids, and these have very high practical importance. Liquids and solids are much more compact than their corresponding vapor or gas phase counterparts and hence, they can't be compressed as much. For this simple reason, the densities of the condensed phases are much greater than their corresponding gases. Since liquids flow easily, this high compressibility of liquids is exploited in the design and functioning of hydraulics, which is crucial in aeronautics, industrial machines, and even in continuously variable car transmissions in modern cars. Condensed phases play a major role in biological systems, providing necessary structural support as well as the circulation of nutrients and removal of waste products. We can't live for more than a few days, for example, without water. Our primary goal in this chapter is to relate the bulk properties of condensed phases with a minimal set of experimental parameters. Based on these properties of condensed phases, we will examine the heat of evaporation, and this process is of the most importance on this planet because it drives our planet's weather system. This process may also be important on other planets that have an atmosphere and oceans. For example, imagine the 385-year-old storm of Jupiter which is still raging across the giant planet, but the cause of the latter is still unknown.[20]

6.2 Kinetic Theory of Liquids and Solids

The kinetic theory states that:

1. The condensed phases are also made of a large number of very small particles, as in a gas, but they have finite volumes, and particles are too close with little space among them.
2. The intermolecular interactions are strong enough to keep the particles in the condensed phase but the particles in a liquid can slip past each other while particles in a solid are held rigidly in their positions.
3. The smaller gaps between the particles in liquids and solids make them difficult to compress, and low coefficients of compression factor and thermal expansion.
4. Weaker interactions and larger gaps among particles of liquids, when compared to those of solids, allow the liquids to flow under the influence of gravity.
5. While liquids occupy a finite volume, they do not have a definite shape, and they take on the shape of the container. While solids have a finite volume, they also have a finite shape, often rigidly held in a crystal lattice.
6. Particles in a liquid have higher thermal energies than particles of the corresponding solid but have less thermal energy than the corresponding gas particles.
7. When sufficient thermal energy is supplied, particles of liquid can escape into the gas. Similarly, particles of a solid can escape into a gas phase or form a liquid when enough thermal energy is supplied.
8. The above phase transitions occur at finite temperatures and transitions are highly cooperative.

Thus, this chapter details equations of state for liquids and solids. We will develop equations that describe the behavior of liquids and solids, based on practical measurements.

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[20] https://en.wikipedia.org/wiki/Great_Red_Spot

6.2.1 Pressure-Volume Relationship

We begin our analysis of the behavior of a liquid as a function of pressure on the liquid at constant temperature and mass. We find that liquids and solids can be compressed when high pressure is applied and there is a measurable decrease in the volume but nothing like gases. This phenomenon is similar to Boyle's law of gases, and we conclude that the volume (V) and pressure applied on the liquid (p) are inversely related (Figure 6.1). The plot shows that volume decreases smoothly with an increase in pressure, and it will be asymptotic along both axes. That is, the volume will approach zero when pressure approaches infinity, and volume approaches infinity when pressure approaches zero. Note that both temperature and mole numbers of the liquid are kept constant. The rise in volume with pressure will be much slower for liquids than for gases but less than that of solids because the condensed phases are harder to compress. This is because the gaps between particles are smaller in a condensed phase than in gases.

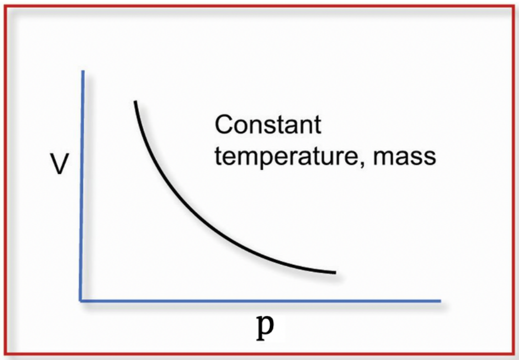

Figure 6.1 Dependence of liquid volume on pressure, at constant temperature and mass.

6.2.2 The coefficient of compressibility

To quantify the above plot in Figure 6.1, we introduce the coefficient of compressibility (κ)(kappa) which is essentially the slope of the tangent drawn to the above curve at any point per unit volume. This has three important details, namely the sign of the quantity, the first term, and the second term, and we will examine each of them here.

$$\kappa = -(1/V)\left(\frac{\partial V}{\partial p}\right)_T$$

The sign of κ is negative because the slope of the above plot is negative at all pressures. This is simply because the pressure and volume are inversely related. If the sign is positive then the volume must increase with pressure, which is not observed in the lab. If the measurement is made with one liter of liquid or two liters or 10 liters of liquid, the slopes will be different and hence, this derivative is not a constant. If we divide the slope with the volume of the liquid, then we normalize the slope per unit volume and is independent of the initial volume of the liquid.

The second term is the change in the volume with an infinitesimal increment in the pressure at constant temperature and mass. This term is the slope of the tangent at any point (first derivative) on the above plot. Thus, we arrive at the above definition for the coefficient of compressibility, and its value for many substances is already known.

6.2.3 p-V relation and the coefficient of compression

We integrate the above differential equation describing how the volume changes with pressure for a condensed phase and obtain a p-V relation by integrating it with appropriate limits. Bringing all pressure terms to one side and all volume terms to the opposite side, we get the necessary expression for integration.

$$-\kappa\, dp = (1/V)\, dV$$

We choose the limits of 1 atmosphere as the lower limit and any pressure p as the upper limit, and the corresponding limits for volume on the right side. Since we are interested in volume change with temperature in the next section, we establish a reference state of volume at 1 atm and any temperature T as V_o^o. Then, the upper limit for volume is to be V_o at pressure p, so that as we change pressure, we arrive at the corresponding V_o values. Now, we integrate the expression with the corresponding limits, shown below, while remembering that temperature is a constant.

$$- \kappa \int_{1\ \text{atm}}^{p} dp = \int_{V_o^o}^{V_o} (1/V)\ dV$$

We get the following expression showing that the volume of a condensed phase decreases exponentially with pressure, explaining the steep curvature of the plot in Figure 7.1.

$$- \kappa\ (p-1) = \ln\ (V_o/V_o^o)$$

This is very different from Boyle's law of gases and these differences became clear only after appropriate mathematical treatment.

A plot of (p-1) vs $\ln(V_o/V^{\circ}_o)$ gives a straight line (Figure 6.2). V_o^o is our reference state at 1 atm pressure, and we are measuring V_o as a function of pressure. This equation is valid for both liquids and solids at constant temperature and mass. Compare this with Figure 6.1 and notice the differences. The slope is negative and is controlled by the value of the coefficient of compressibility, κ. The relation is logarithmic, but its decrease is slower than the inverse relation of Boyle's law, and this is because the condensed phases are much harder to compress than gases. This is in turn because gases have large empty spaces in them, but the condensed phases do have some empty spaces but much less.

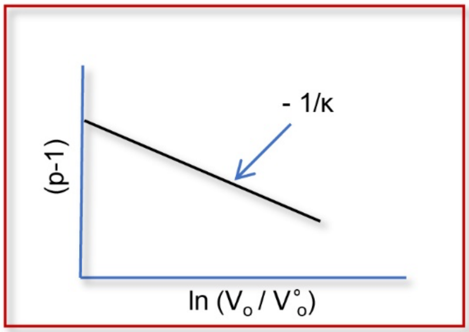

Figure 6.2 Plot of (p-1) vs ln V_o/V°_o, at constant T and Mass, the slope is related to the compressibility factor.

One drawback of the above equation for compressibility is that the value of the coefficient of compressibility is characteristic of a given condensed phase, and hence, this equation is specific for a given substance. That is, we need to use the corresponding coefficient of compressibility for each substance to write separate equations, like the van der Waals equation. Thus, empirical relations such as these have some limitations, but it is our best approach to understand the behavior of the condensed phases, thus far. This is our first part of the equation of state and next, we will examine the effect of temperature on the volume of the condensed phase, at constant pressure and mass.

6.2.4 Temperature-Volume relationship for a condensed phase

We will examine the temperature dependence of the volume of a condensed phase, and this is analogous to the Charles law of gases. We recognize that most liquids and solids expand with an increase in temperature. That is, the volume of a condensed phase increases with an increase in temperature, thermal expansion, under constant pressure and mass conditions (Figure 6.3). To quantify this behavior, we will introduce the coefficient of thermal expansion, analogous to the coefficient of compressibility discussed above.

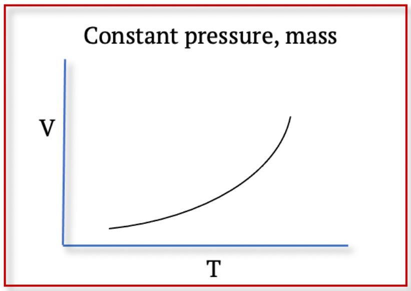

Figure 6.3 Thermal expansion of a liquid at constant pressure and mass.

6.2.5 The coefficient of thermal expansion

The curve in Figure 6.3 shows the experimental data for a condensed phase, and the slope of the tangent is changing as we change the temperature. Therefore, the coefficient of thermal expansion (α)(alpha) is defined as the slope of this line per unit volume and given by the equation below. Slope per unit volume is used here, for the same reasons we discussed with the coefficient of compressibility. That is, the slope is different at different volumes and hence, when we divide the slope with the volume at that point, we get a constant or change in volume per unit volume per unit change in temperature. Thus, α is defined as given below.

$$\alpha = (1/V)\left(\frac{\partial V}{\partial T}\right)_p$$

Note that we have defined α the same way for gases, previously. This is the infinitesimal change in volume per liter when the temperature is raised by an infinitesimal amount, at constant pressure and mass. Also, note that there is no negative sign in front of the derivative because the slope is positive throughout the plot. That is, volume increases with temperature, except for water, which is a special case. In the case of water, when the temperature is increased from 0 to 4 ˚C, the volume decreases. This is due to the complex network of hydrogen bonds that are broken with the increase in temperature, and the volume of water decreases until this point.[21] This is also referred to as the anomalous expansion of water. But, for most of the other substances we know, the above equation is valid, and integration of this equation provides a relationship between volume and temperature of the condensed phase.

6.2.6 V-T relation and thermal expansion

We rearrange the above equation to bring all temperature terms to one side and the volume terms to the opposite side, and we recognize that α is constant (independent of V and T), and we are also keeping pressure and mass constant as well. Thus, we get the following relation.

$$\alpha\, dT = (1/V)\, dV$$

Now, we choose the appropriate limits to integrate this expression and combine it with the previous p-V relation we obtained. We can define T_o and V_o as the lower limits, and T and V as the upper limits for the two integrals. This will give us an expression that connects T and V with T_o and V_o, which is convenient to combine with the p-V equation derived above.

$$\alpha \int_{T_o}^{T} dT = \int_{V_o}^{V} (1/V)\, dV$$

The integration with the above limits gives us the relation shown below, which is also a surprise because it is unlike the linear relationship we discussed under Charles' law.

$$\alpha\,(T - T_o) = \ln\,(V/V_o)$$

$$\ln V = (\ln V_0 - \alpha\, T_o) + \alpha\, T$$

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[21] https://www.quora.com/Water-What-is-the-scientific-reason-for-the-anomalous-expansion-of-water

This equation is like the p-V relation we got for the condensed phases, with some important differences and some similarities. In the p-V equation κ appears which is replaced by α in the T-V equation. There is no negative sign here, but the volume increases logarithmically with temperature. As mentioned previously, the positive sign in the coefficient of expansion indicates a positive slope and an increase in V with an increase in T (Figure 6.4). This logarithmic relation contrasts with Charles' law, and again, the smaller increase in V with T for the condensed phases is due to the strong cohesive interactions between the particles of the condensed phases and smaller gaps between them. This contrasts with the weak interactions in a real gas or no interactions in the case of an ideal gas and large intermolecular distances. Thus, the distinction between the gases and the condensed phases is very clear from these expressions.

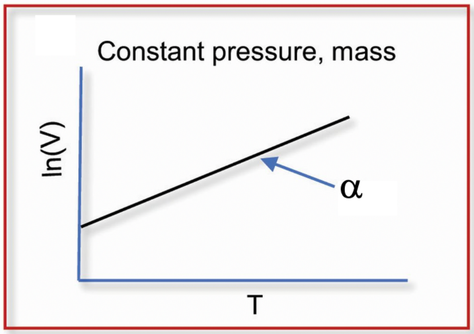

Figure 6.4 Linear plot of ln V vs T for a condensed phase and the slope is the volume coefficient of thermal expansion.

Example 6.1

An interesting side story on thermal expansion is regarding the stealth spy plane, nicknamed the Blackbird of the US Air Force.[22] It traveled at an amazing speed greater than three times the speed of sound, but this created friction with the surrounding air, and the canopy temperatures often exceeded 300 ˚C during the flight. Account for the thermal expansion of the canopy, at these high temperatures, which is made of 92% titanium, gaps were left in the canopy panels to accommodate expansion. A side story is that the titanium needed not available in the US and had to be procured from the Soviet Union through a dummy company. Ironically, the plane was used for high altitude recon on Russia and due to its high speed, the plane outran Soviet missiles.

Example 6.2

Continuing the story in Example 1 on the stealth aircraft, the plane leaked fuel on the ground because of the gaps in the canopy allowing thermal expansion. Thus, it had to be refueled mid-air, immediately after takeoff. To avoid fire on the ground due to the leaking fuel, a special jet fuel that is thermally stable was created, but it was hard to light the stable fuel to start the engines and created another problem. To light the stable fuel, triethyl borane was injected initially into the engines, which ignites on contact with air. The pilots and the crew had to wear special suits to protect them when they exited the hot plane on landing. This supports the fact that we need to account for the coefficient of thermal expansion which is an important consideration in technology.

Our next task is to combine these pressure and temperature equations to obtain the equation of state for the condensed phases. That is, we will obtain a function of pressure, temperature, and volume at constant mass, for condensed phases, which will be analogous to the ideal gas law for gases.

Example 6.3

For a liquid, the following data were obtained the V/L values of 10, 40, 100, 400 at the corresponding temperatures t/˚C as 593, 673, 736 and 844, respectively. Calculate its coefficient of thermal expansion.

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[22] https://en.wikipedia.org/wiki/Lockheed_SR-71_Blackbird

Take any two pairs of values and obtain the slope. Use ($\ln V_1 = a + b T_1$) and ($\ln V_2 = a + b T_2$) or $\ln V_1 - \ln V_2 = b (T_1 - T_2)$, where a and b are constants, and we get intercept b as:

$$b = \frac{\ln(V1/V2)}{T1 - T2} = \frac{\ln\frac{10\ L}{400\ L}}{(593 + 273.15 - 844 - 273.15)K} = \frac{-3.69}{-251K} = 0.0147\ /K$$

6.2.7 Combined effect of both pressure and temperature on volume, at constant mass

We combine the pressure and temperature equations by connecting them with the initial volume V_o, which is common in both the equations, as reproduced below.

$$-\kappa\,(p-1) = \ln(V_o/V_o^o) \quad \text{and} \quad \alpha\,(T - T_o) = \ln(V/V_o)$$

But first, we will write the logarithmic functions as the corresponding exponential functions for simplification, as follows.

$$V_o = V_o^o\, e^{-\kappa(p-1)} \quad \text{and} \quad V = V_o\, e^{\alpha(T-T_o)}$$

We recognize that the numerical values of both α and κ are very small (Table 6.1), and in such a case, the exponential functions can be approximated to linear functions which are much easier to combine. When the exponent is close to zero, the exponential function is expanded as a linear function with the first two terms ($e^x = (1+x)$), with the higher order terms being too small to consider.

$$V_o = V_o^o\,[\,1 - \kappa\,(p-1)] \quad \text{and} \quad V = V_o\,[\,1 + \alpha\,(T - T_o)]$$

By substituting for V_o from the first equation (left) into the second equation (right), we get the combined equation as below.

$$V = V_o^o\,[\,1 - \kappa\,(p-1)]\,[\,1 + \alpha\,(T - T_o)]$$

This is the equation of state for condensed phases, both liquids, and solids, at constant mass, and this equation is specific for a given substance because the coefficient of compressibility and the coefficient of thermal expansion vary from substance to substance. Despite that, the equation is of considerable value when once the constants are measured experimentally for a substance of interest.

6.2.8 Significance of the equation of state for condensed phases

We recognize that liquids and solids are certainly more complex when compared to gases and use the approximation that the exponent of the exponential functions are very small, both the pressure and temperature functions are expanded as linear equations. Thus, we introduced approximations to simplify otherwise complex functions. As we combined the two equations, we have a more complicated expression than the ideal gas law, and it has two experimental parameters that are characteristic of the substance which need to be measured for each substance. For all practical purposes, V decreases linearly with an increase in pressure, unlike Boyle's law, and ln(volume) increases linearly with temperature unlike in the case of Charles' law. Thus, we see significant differences in the behavior of condensed phases from the gases.

6.2.9 Values of α and κ for some liquids and solids

The coefficients of compressibility (κ) and thermal expansion (α) for a few substances are given in Table 6.1. We recognize that sodium chloride has a much larger coefficient of thermal expansion than quartz and because of this, when you heat salt crystals they start to crackle or explode gently. The coefficient of thermal expansion for liquids such as mercury is high enough to be used in thermometers, but we do not do this anymore due to its high toxicity. For comparison, benzene has almost six times larger coefficient of thermal expansion than mercury, but benzene is highly carcinogenic. Recognize that liquids expand much more than solids. This is due to weaker intermolecular interactions in liquids than in solids and is reflected in their respective coefficients of thermal expansion.

Table 6.1 Values of α and κ for a few samples

Symbol	*Quartz*	*Cu*	*NaCl*	*Hg*	*H_2O*	*C_6H_6*
$\alpha/(10^{-4}\ K^{-1})$	0.15	0.49	1.21	1.81	2.07	12.4

κ / (10^{-6} atm^{-1})	2.8	0.78	4.2	3.85	45.3	94

The coefficient of compressibility also differs among these substances, significantly. For instance, liquids can be compressed more readily than solids due to the extra space available in liquids. It is much harder to compress mercury than benzene for similar reasons. It is quite difficult to compress copper when compared to water and these are important for practical applications of these substances.

6.3 Vapor Pressure of a Condensed Phase

We recognize that both solids and liquids can coexist with their vapors at any temperature of their existence, while liquids will be in equilibrium with the corresponding solids only at their melting temperature. Most solids and liquids evaporate to some extent and the vapor pressure depends on the heat of vaporization of the substance. That is, energy is required to overcome the cohesive forces of the condensed phase and transfer the particles from the condensed phase into the vapor phase. To gain insight into the forces that keep them in the condensed phase, we look at the effect of temperature on the vapor pressure. For example, the diagram in Figure 6.5 shows a condensed phase in a closed container. Let us say that we have no vapor in the headspace initially, and as time progresses, at a given temperature and pressure, space above begins to fill with the vapor and ultimately saturates the headspace. At equilibrium, the rates of vapor condensation back to the condensed phase and liquid evaporation or sublimation of the solid into the vapor phase are exactly equal.

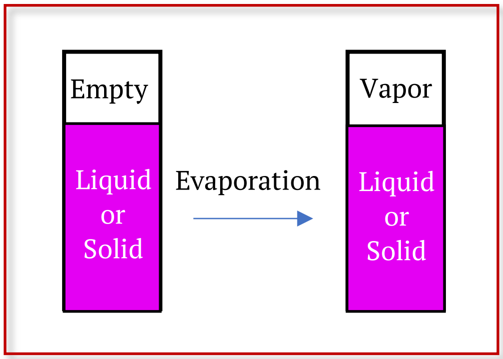

Figure 6.5 Evaporation of liquids and solids, under standard conditions.

That means, certain liquid molecules are continuously escaping into the vapor phase and certain vapor molecules are continuously condensing back to the liquid phase. Thus, a dynamic equilibrium is established between the two phases. When the container is open, the vapor molecules escape to the outside and the liquid will continue to evaporate until there is no more liquid left behind in the container. We can attest to this experience in our daily lives.

The same phenomenon also occurs with solids, even though it is much less dramatic, mostly. We never see a stone evaporate in our lifetime, but certain solids such as camphor or iodine evaporate rather rapidly. Let's say that you have iodine enclosed in a container and that initially there is no vapor in the space above the solid. As time progresses, some of the iodine molecules from the solid escape into the vapor phase, and the gas above the solid turns from colorless to faint violet color. This phenomenon is normally referred to as sublimation analogous to boiling, which is loosely defined as the escaping of the molecules from the solid phase directly into the vapor phase without passing through a liquid state. Several organic materials exhibit this property and indeed, organic chemists exploit this property of volatile solids for purification by sublimation.

When you start warming up the liquid in the container at 1 atm, it begins to boil when the vapor pressure of the liquid is equal to that of the atmospheric pressure (1 atm) above it, and this temperature is its normal boiling point. The normal sublimation point of a solid, analogously, is the temperature when the vapor pressure of a solid is exactly equal to the pressure applied on it (1 atm).

6.3.1 Cohesive energies of liquids and solids

Liquids and solids have particles that are kept much closer than in the gas phase and van der Waals attractive forces are strong enough at these shorter distances to hold them together. When the kinetic energy is enough to overcome these attractive forces, they escape into the vapor phase. The thermal energy needed to overcome the cohesive forces of the liquid is quantified by examining the excess energy of the vapor particles when compared to those in the liquid phase. This is the energy needed to bring the molecule from the liquid phase into the vapor phase. We will use the barometric law to estimate this quantity because the relation holds not only for the potential energy of the particles at different heights of a gas column but also for the potential energy of the molecules in the vapor phase with respect to the liquid phase. We recognize the barometric law as follows, where p is the pressure at some height z when subjected to the gravitational field and acceleration due to gravity g and molar mass M.

$$p = p_o\, e^{-(Mzg/RT)}$$

This equation relates the pressure to the potential energy of the molecule at height z of the column because Mzg is the potential energy at height z. We argue that the same expression can be used to construct the energy of the vapor molecules because we are moving the molecules from a low energy liquid surface to a higher energy vapor phase, analogous to the gas column in the gravitational field. The energy required to move this way is equivalent to the potential energy of the vapor molecules with respect to the liquid phase.

6.3.2 Measurement of the heat of vaporization

We recognize that the potential energy of the vapor is essentially the heat of vaporization, as the height of the gas column is of no concern here. We introduce B as the proportionality constant, Q_{vap} is the heat of vaporization and the negative sign in the exponent ensures that the vapor pressure decreases with an increase in Q_{vap}. Thus, a modification of the Boltzmann distribution (barometric law) is sufficient.

$$p = B\, e^{-(Q_{vap}/RT)}$$

Later, we will recognize that this is also the enthalpy of vaporization and the energy of the molecules in the vapor phase is indeed, enthalpy not internal energy. These energy concepts will be introduced in the next chapters, but it is useful to connect with them in this context. We replace the proportionality constant with maximum vapor pressure (p_∞) because at large values of T, the exponential approaches 1 and $p=p_\infty$.

$$p = p_\infty\, e^{-(Q_{vap}/RT)}$$

By taking natural logarithms on both sides, we get the following linear relation that can be tested experimentally and obtain the heat of vaporization of volatile substances.

$$\ln p = \ln p_\infty - (Q_{vap}/RT)$$

Vapor pressure is related to temperature in an interesting manner. As the temperature increases, the value of 1/T decreases and we subtract less value from the maximum pressure, p_∞. Thus, the vapor pressure increases with an increase in temperature, which is not immediately obvious, but examining both terms on the right of the equation we can see why. A plot of ln(p) vs 1/T is shown in Figure 6.6, and the slope is negative with an intercept equal to maximum possible vapor pressure, p_∞. The slope of the straight line is equal to $-Q_{vap}/R$ and hence, the heat of vaporization can be determined without using a calorimeter. This is a unique example of measuring enthalpies without a calorimeter.

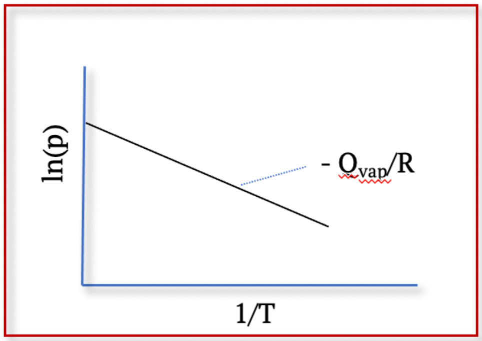

Figure 6.6 Plot of the natural logarithm of vapor pressure as a function of inverse temperature and the non-calorimetric determination of the heat of vaporization (Q_{vap}) of a liquid or a volatile solid.

Another unique feature of the above plot is that we can calculate the temperature where the vapor pressure corresponds to 1 atm, the normal boiling point of the liquid, or the normal sublimation point of a volatile solid. Thus, a series of vapor pressure measurements as a function of temperature provides both the heat of vaporization as well as the normal boiling point for a liquid or the normal sublimation point of a volatile solid. This is a convenient method to estimate the high boiling points of some liquids without measuring them directly or when it is difficult to reach such high temperatures.

Table 6.2 Values of enthalpies of vaporization and their normal boiling points (Bp) for a few samples

Symbol	*Methane*	*Ammonia*	*Methanol*	*H_2O*	*Al*	*Fe*
Q_{vap}/ (kJ mol^{-1})	8.17	23.35	35.2	40.66	294.0	340.00
Bp/ (K)	112	240	338	373.15	2792	3134

The enthalpies of vaporization of a few substances are given in Table 6.2, and a comparison gives further credence to the discussions above. Indeed, the boiling points of several liquids correlate nicely with their heats of vaporization where the intermolecular interactions are similar in origin. For example, the first 4 examples in the table above follow a roughly linear trend, while the homologs of alkanes show a strong linear correlation. But significant deviations are noted among others where metallic bonds or other strong interparticle interactions dominate, as in the cases of liquids of Al and Fe, shown above.

Example 6.4

For liquid zinc, the following data were obtained, vapor pressure, p/mm Hg: 10, 40, 100, 400 for the corresponding temperatures, t/˚C: 593, 673, 736, 844, respectively. Calculate the heat of vaporization and its normal boiling point.

Plot ln p vs T and obtain the slope and intercept. Using the equation ln p - $\ln p_\infty$ = - (Q_{vap}/RT), get the heat of evaporation and $p_{infinity}$.

Let ln p = ln a + b/RT where b = - Q_{vap}, then $\ln p_1 - \ln p_2 = \ln(p_1/p_2) = b(1/RT_1 - 1/RT_2) = b(1/R)[(T_2-T_1)/(T_1T_2)]$

$$b = \frac{\mathrm{RT_1\ T_2}\ \ln(p_1/p_2)}{(T_2 - T_1)} = \frac{8.31\,J\,(593 + 273.1)K(844 + 273.15)K\ \ln\frac{10\ mmHg}{400\ mmHg}}{mol\ K\ (844 + 273.15 - 593 - 273.15)K} = -118.2\ kJ/mol$$

$$Q_{vap} = -b = 118.2\ \text{kJ/mol}$$

Normal boiling point is when the vapor pressure = 1 atm or ln p = 0. $(R/Q_{vap})(\ln(p_1/p_2))+(1/T_1) = 1/T_2$

$$\frac{1}{T_2} = \left(\frac{1}{T_1}\right) + \left(\frac{\mathrm{R}}{Q_{vap}}\right)\ln\frac{p_1}{p_2} = \frac{1}{(593 + 273.1)K} + \frac{8.31\,J/\,mol\ K}{118200\,J/mol}\ \ln\frac{10\ mm\ Hg}{760\ mm\ Hg}\ or\ T_2 = \cdots ....$$

6.4 Molecular interpretation

The shallow dependence of volume on pressure and temperature for condensed phases when compared to the gases is due to the lesser volume available in the condensed phases when compared to those of the gases. The volume change is small enough that we can approximate its function from that of an exponential to a linear one. However, notice that these functions are different from Boyle's law or Charles' law. In addition to the lesser volume available for compression, the stronger intermolecular forces in the condensed phases reduce their thermal expansion as well. Thus, we can qualitatively conclude that the coefficient of compressibility depends on the volume available for compression, while thermal expansion is inversely related to the strength of intermolecular forces. Thus, the greater the thermal expansion, the weaker the intermolecular forces are expected to be. The values of these experimental constants for condensed phases provide insight into the molecular details of these substances.

So, what's happening at the molecular level when you heat a liquid or a solid? When you heat a liquid or a solid, we determined in the previous discussions that the kinetic energy of the sample is increasing, which means that the molecules are traveling at higher and higher velocities. Boltzmann distribution tells us that some of them will have high enough kinetic energies to escape the condensed phase into the vapor phase. The higher the temperature, the greater this fraction would be. Eventually, at some point, the vapor pressure equals that of the external pressure on the system and this is the boiling point.

Boiling point is an interesting phenomenon, because the conversion of the liquid phase to the vapor occurs at a constant temperature, even though evaporation can occur at all different temperatures of the liquid. The constant boiling temperature is because all the excess energy supplied to the system is used up in lifting the molecules from the liquid phase to the vapor phase and the temperature does not rise. At this temperature, the cohesive forces in the liquid can no longer hold the molecules in the liquid phase and all available energy is used to release them into the vapor phase. This is a phase transition, where the thermal energy of the system and the cohesive forces holding the molecules together are perfectly matched.

When condensation happens, the reverse process is taking place where some vapor particles no longer have high enough energy to stay in the vapor phase and condense into a liquid or even a solid.

6.5 Applications in daily life

The low compressibility of solids is very useful for practical applications in the construction of skyscrapers, dwellings, trains, machines, and other durable goods. On the other hand, the low compressibility of the liquids coupled with their ability to flow is exploited as in hydraulics for aeronautics and in heavy equipment. These days, the continuously variable transmission in automobiles, instead of the conventional power train, utilizes hydraulic fluids and provides a smoother ride as the gears are shifted continuously. Thus, the compressibility coefficients of condensed phases are important for applications in engineering and technology. Similar is the situation with the property of low thermal expansion of liquids and solids.

Since the iron rails of the railroad expand in summer and shrink in winter, they are separated at the ends to account for the coefficient of thermal expansion. You will also find that large panels of bridges and even buildings are joined together with gaps between them to account for thermal expansion. The electric trains that use overhead wires were suspended during the heat waves of many summers in the Northeast Corridor of the US. This is because the thermal expansion of the wires caused them to hang too low for the trains to run safely.

Anomalous expansion of water is responsible for the survival of the fish during the harsh winters of North America, due to this expansion, ice is lighter than water at its normal melting point. Thus, lakes are covered with ice on top while liquid water can exist underneath, and this fact played a key role in the evolution of biological life on this grand planet.[23]

The phenomenon of liquid evaporation plays a very important role on our planet, which is covered with water on much of its surface. Even though the oceans and lakes do not boil, normally, the water continues to evaporate from their surface and eventually produces clouds and rain. The entire weather system is driven by this major phase transition on our planet, and we note that the cloud formation and rain formation are the same phase transition, each of them occurring in opposite directions. Thus, one could say, evaporation is an important phenomenon in our daily life.

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[23] https://www.explainthatstuff.com/water.html

In addition to the weather, there are other examples of this phenomenon in our daily lives as well. For example, the evaporative cooling of water is used in desert coolers to cool the air that is forced through a wet filter. There is a new kind of refrigerator working on this principle to keep its contents at 4˚C without using any electrical power. The leaves of plants use evaporative cooling to keep their temperatures regulated on a hot summer day. The powerful steam locomotive that has driven the industrial revolution of the bygone era, took advantage of the conversion of liquid water to steam and utilized the steam energy to power various machines to produce goods. Ironically, this same process is still being used with some modifications to run steam turbines and produce electricity, even now.

Organic chemists use the conversion of liquid to vapor phase at the constant boiling point to purify volatile liquids by distillation and similarly, they use sublimation to purify volatile solids. The entire wine and liquor industry depends on distilling ethanol from its less desirable components. The entire petroleum industry thrives on the distillation of crude oil into its numerous fractions, for practical applications. Thus, this humble phase transition from the condensed phase to the vapor phase has become ubiquitous in our lives.

6.6 Key points

1. The equation of state for condensed phases requires the determination of the parameters α and κ, but it can predict the pressure and temperature variations of condensed phases.
2. This equation of state is analogous to the ideal gas law, but it needs to be tailored for each substance, just like the van der Waals equation.
3. Most liquids expand on heating except for water with its anomalous expansion between 0 and 4 ˚C, and most solids expand except for graphene and silicon which shrink on heating.
4. Molecules in the condensed phases require a certain amount of energy to escape into the vapor phase and this is the enthalpy of vaporization or enthalpy of sublimation, important to the food and perfume industry.
5. When the vapor pressure equals 1 atm, the temperature is the normal boiling point of the liquid.
6. When the vapor pressure equals the external pressure on the solid, the temperature is the sublimation point of the solid. When the external pressure is 1 atm, this is the normal sublimation point.
7. The heat of evaporation is obtained by examining the vapor pressure as a function of temperature, without using a calorimeter.

6.7 New terms and units

$$\alpha = (1/V)\left(\frac{\partial V}{\partial T}\right)_p \qquad \kappa = -(1/V)\left(\frac{\partial V}{\partial p}\right)_T \qquad \ln p = \ln p_\infty - (Q_{vap}/RT)$$

$$\ln V = (\ln V_0 - \alpha T_o) + \alpha T \qquad V = V_o\ [1 + \alpha (T - T_o)] \qquad V_o = V_o^o\ [1 - \kappa (p-1)]$$

Coefficient of compressibility, coefficient of thermal expansion, heat of evaporation, normal boiling point, vapor pressure and normal sublimation point. Inverse temperature is the unit of α while κ has the units of inverse pressure. The heat of evaporation has the units of molar energy, or kcal/mol, and vapor pressure has the units of pressure.

6.8 Self Reflection

1. Imagine the pond in your backyard freezing in the winter in North America. Why does the pond freeze from the top to the bottom but not from the bottom to the top?
2. Construct a device that uses the thermal expansion of solids to measure temperature.
3. Give a molecular description of why water has the highest density at 4 ˚C but not at 0 ˚C.
4. Recent studies indicate that the release of water vapor from the landmass on earth increased by 10% in recent years. If this is entirely due to a rise in the land temperature, what is the average increase in the land temperature over this period?
5. Why is the equation of the state of the condensed phases not followed by gases?
6. What is the major molecular level difference between solids and liquids?
7. What would be the molecular explanation for the shrinking of a substance on heating?

8. Plot the heat of evaporation[24] as a function of normal boiling points of several liquids[25] and comment on your observations if the plot is linear or non-linear.

6.9 Further Reading

1. https://en.wikipedia.org/wiki/Thermal_expansion
2. https://en.wikipedia.org/wiki/Compressibility

6.10 Self Tests

1. What are the units of compressibility factor k ("Kappa") for liquids?
   - a. kg/cm^2
   - b. N/m^2
   - c. $kg/m\ s^{-2}$
   - d. atm^{-1}
   - e. none of the above
2. What are the units for the coefficient of thermal expansion?
   - a. K^{-1}
   - b. atm^{-1}
   - c. N/m^3
   - d. ˚C
   - e. none of the above
3. Most liquids expand upon heating with the exception of _______.
   - a. alcohol
   - b. toluene
   - c. water
   - d. oil
   - e. none of the above
4. A plot of ln (Volume) versus temperature for a condensed phase at constant pressure and mass will give _______function with a positive slope.
   - a. a single exponential
   - b. a double exponential
   - c. a linear
   - d. a polynomial
   - e. none of the above
5. The coefficient of thermal expansion can be calculated from the slope of which kind of plot?
   - a. V vs. T, constant pressure
   - b. ln (V) vs. T, constant pressure
   - c. p vs. T, constant volume
   - d. ln (p) vs. T, constant volume
6. Liquids are more readily compressed than solids.
   - a. True
   - b. False
   - c. cannot predict
   - d. none of the above
7. For a liquid, the following data were obtained. Calculate its coefficient of thermal expansion.

Volume (L)	*10*	*40*	*100*	*400*
Temperature (K)	593	673	736	1233

   - a. 1.6 atm^{-1}
   - b. 2.7 x 10^{-3} K^{-1}
   - c. 1.6 K^{-1}
   - d. 2.7 x 10^{-3} atm^{-1}
   - e. none of the above
8. The slope of a plot of ln(vapor pressure) vs. 1/T for liquid-vapor equilibrium is equal to

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[24] https://www.engineeringtoolbox.com/fluids-evaporation-latent-heat-d_147.html

[25] https://www.engineeringtoolbox.com/boiling-points-fluids-gases-d_155.html

a. $-V_{vap}/R$
b. $-Q_{vap}/T$
c. $-Q_{vap}/R$
d. Q_{vap}/R

9. Vapor pressure of a liquid ________ with increase in temperature.
a. stays constant
b. increases
c. decreases
d. cannot tell
e. none of the above

10. The Y-intercept of a plot of ln(vapor pressure) on the Y-axis vs. 1/T on the X-axis for vapor-liquid equilibrium is
a. maximum possible vapor pressure
b. minimum possible vapor pressure
c. normal boiling point
d. heat of vaporization
e. none of the above

11. Most liquids ________ upon heating.
a. expand
b. constrict
c. do not change volume
d. boil
e. can't say

12. A plot of ln (volume) versus temperature for a condensed phase at constant pressure and mass will give a linear function with a ________slope.
a. positive
b. decreasing negative
c. increasing positive slope
d. changing
e. constant negative slope

13. When pressure on a liquid is increased, its volume
a. increases linearly
b. decreases linearly
c. stays the same
d. decreases logarithmically
e. none of the above

14. Which one of the following is the correct equation for the coefficient of volume expansion of a liquid as a function of pressure at constant temperature?
a. $\kappa = -(1/V)\left(\frac{\partial V}{\partial T}\right)_p$
b. $\kappa = (1/V)\left(\frac{\partial V}{\partial p}\right)_T$
c. $\kappa = -(1/V)\left(\frac{\partial p}{\partial V}\right)_T$
d. $\kappa = -(1/V)\left(\frac{\partial V}{\partial T}\right)_p$
e. none of the above

15. Which of the following describes describes the relation between volume and pressure of a liquid, at constant temperature?
a. $-\kappa\,(p+1) = \ln (V_o/V_o^o)$
b. $-\kappa\,(p-1) = \ln (V_o/V_o^o)$
c. $-\kappa\,(po-1) = \ln (V_o/V_o^o)$
d. $\kappa\,(p-1) = \ln (V_o/V_o^o)$
e. $-\kappa\,(p-1) = (V_o/V_o^o)$

16. Which of the following defines the coefficient of thermal expansion of a liquid at constant pressure?
a. $\alpha = (1/p)\left(\frac{\partial V}{\partial T}\right)_p$

b. $\alpha = - (1/V) \left(\frac{\partial V}{\partial T}\right)_p$

c. $\alpha = (1/V) \left(\frac{\partial V}{\partial T}\right)_p$

d. $\alpha = (1/V) \left(\frac{\partial V}{\partial T}\right)_T$

e. $\alpha = (1/V) \left(\frac{\partial p}{\partial T}\right)_V$

17. Which one of the following is the equation of state for a liquid?

a. $V = p_o^o [1- \kappa (p-1)] [1 + \alpha (T - T_o)]$

b. $p = V_o^o [1- \kappa (p-1)] [1 + \alpha (T - T_o)]$

c. $V = V_o^o [1+ \kappa (p-1)] [1 + \alpha (T - T_o)]$

d. $V = V_o^o [1- \kappa (p-1)] [1 + \alpha (T - T_o)]$

e. $V = V_o^o [1- \kappa (p+1)] [1 + \alpha (T - T_o)]$

18. Which one of the following is the equation of state for a solid?

a. $V = V_o^o [1- \kappa (p-1)] [1 + \alpha (T - T_o)]$

b. $V = V_o^o [1- \kappa (V-1)] [1 + \alpha (T - T_o)]$

c. $V = V_o^o [1- \kappa (p-1)] [1 + \alpha (T + T_o)]$

d. $V = V_o^o [1- \kappa (p+1)] [1 + \alpha (T - T_o)]$

e. $V = V_o^o [1 - \kappa (p-1)] [1 - \alpha (T - T_o)]$

19. Which of the following is true?

a. Liquids are more compressible than solids because these molecules can be squeezed more readily

b. Liquids are more compressible than solids because these molecules are softer

c. Liquids are less compressible than solids because these molecules are hard

d. Liquids are more compressible than solids because they have larger voids between the molecules than solids

e. none of the above

20. Blackbird aircraft leaked fuel on the ground because its canopy metal sheets had gaps to account for:

a. volume expansion of air in the cockpit

b. pressure expansion of the canopy as it flew high altitudes

c. thermal expansion of the canopy at high speeds

d. light weight of the aircraft

e. none of the above

21. Which of the following accounts for change in vapor pressure of a liquid with temperature?

a. $p = B\, e^{-(Q_{vap}/RT)}$

b. $p = p_\infty\, e^{-(Q_{vap}/RT)}$

c. $\ln p = \ln p_\infty - (Q_{vap}/RT)$

d. all the above

e. none of the above

6.11 Self Tests Key

1. d, 2. a, 3. c, 4. c, 5. a, b, 6. b, 7. b, 8. c, 9. b, 10. a, 11. a, 12. a, 13. d, 14. e, 15. b, 16. c, 17. d, 18. a 19. d, 20. c, 21. d

6.12 Problems

1. For a liquid, the following data were obtained. Calculate its coefficient of thermal expansion. (Ans. $2.7 \times 10^{-3}\ K^{-1}$)

Volume (L)	*10*	*40*	*100*	*400*
Temperature (K)	593	673	736	1233

2 Using the coefficient of volume expansion of water (0.000249/K), calculate its final volume when 22.4 L is heated from 273.15 K to 350.00 K. (Ans. 22.83 L)

3 In old days, the clinical thermometers used thermal expansion of mercury. If the temperature change is from 25 ˚C to 38 ˚C, what is the minimum volume of mercury needed to obtain 0.2% change in its volume (Ans. 0.1 mL)

4 The compressibility factor of petroleum is $1x10^{-6}$ psi. If it is pumped (density of 800 kg/m^3) from a well of 2 km deep to the surface, what is the percent increase in its volume on arrival at the surface? (Ans. 0.023%)

5 The coefficient of thermal expansion of gasoline is 0.00095/K. If a car has a tank of 20 gallon capacity and during a summer day the gas is heated by as much as 10 K. How much extra space in liters is to be kept in the tank so that it does not overflow on warming up? (Ans. 0.719 L)

6 A desert cooler operates by forcing air through a filter that is kept wet by water. As the water evaporates it cools the air due to heat of vaporization sourced from the air. If the cooler consumes 5 gallons of water a day, what is the maximum cooling capacity of the cooler? (Hing: the cooling capacity is defined as kJ of heat removed from air per day, Ans. 42,479 kJ/day)

7 The humidifier used in your home in winter months works by making fine mist of water droplets. As the droplets evaporate, they absorb heat from the surroundings and increase the humidity. If the humidifier consumes 1 L of water a day, what is the heat loss due to evaporation and how much would that add to your heating bill per month (31 days) in US Dollars, if each MJ of energy costs one penny? (Ans. 0.7 $)

Chapter 7. The Zeroth Law

After completing this chapter, you will be able to:

- Recognize the Zeroth law of thermodynamics and define temperature in a practical manner.
- Synthesize the thermometric equation and construct specific temperature scales.
- Synthesize an experimental method to quantify temperature.
- Recognize the constant volume and the constant pressure thermometers.
- Recognize the absolute scale of temperature and define the absolute zero from it.

Goals

- We will examine heat flow across objects that are in contact and at different temperatures.
- Using simple mathematical manipulations, we will arrive at the thermometric equation and examine the constant pressure and constant volume thermometers.
- We will recognize the thermodynamic definition of temperature and establish the absolute scale of temperature with the definition of absolute zero temperature.

7.1 Why Study this?

The zeroth law provides a basis for temperature measurement. For example, we thermally equilibrate the thermometer of our choice with the object under investigation and determine the temperature reading. This is only possible if the temperatures of the object and the thermometer are equal when thermal equilibrium was achieved. This is the essence of the zeroth law, guaranteeing that the two temperatures of the objects are the same at thermal equilibrium. To better understand this feature, assume for a moment that this law is not valid. The whole world will plunge into chaos. We will not be able to make even the simplest measurement or predict the weather or determine if a person is sick with fever and so on. The measurement temperature is so critical to our civilization, science, and technology that it demands a full investigation at a fundamental level. This law also defines temperature and is important for all our discussions of thermodynamics (flow of heat or dynamics of heat). Our discussion also sets the lowest temperature achievable in the whole of the universe, which makes it very interesting to investigate this law.

7.2 The Zeroth Law

We will define what temperature is and determine a quantitative method to measure it on the absolute scale.[26] Temperature is usually considered as the degree of hotness of an object. This kind of definition is not analytical and not useful for making measurements in the laboratory. We will define temperature in a practical way, as a measurable quantity in the following manner. But first, we need to examine what is thermal equilibrium.

7.2.1 Thermal Equilibrium

We will use one of the many properties of gases to measure temperature. We choose gases for this because we understand gases much better than liquids or solids. We have previously examined how the temperature of the gas, its pressure, mass, and volume are interrelated. Consider two gas samples in two separate containers, which are at two different temperatures (Figure 7.1 A., left). Then we bring them together in thermal contact (Figure 7.1 B., right). Let the blue sample be at pressure p_1, have volume V_1, at temperature T_1, and a fixed number of moles. Let the red sample have the pressure p_2, volume V_2, and temperature T_2 with a fixed number of moles. Let $T_1 > T_2$, so that the blue object is warmer than the red object. This is the degree of hotness from practical experience, but we will go beyond this. Let the two samples be equipped with pressure gauges so that we can monitor the pressures of each of these samples at any time.

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[26] https://en.wikipedia.org/wiki/Kelvin

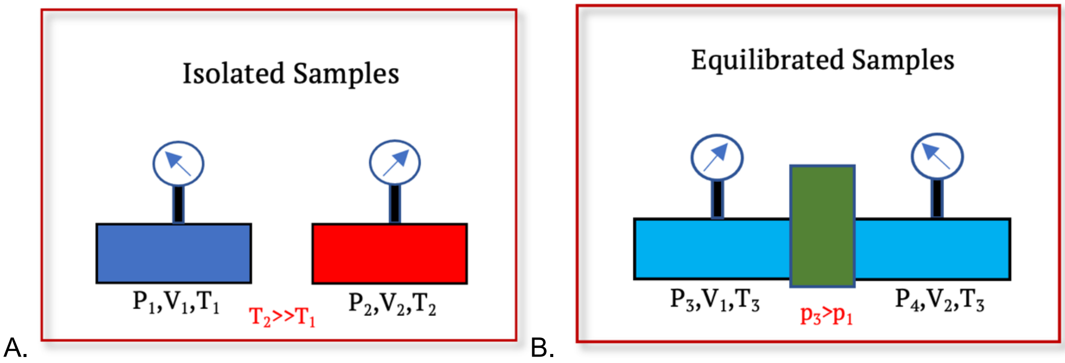

Figure 7.1 A. Gas samples at different temperatures (T_1 and T_2) are isolated (left) and B. When brought to a thermal equilibrium, where both samples have the same temperatureT_3 (right).

When these objects are in thermal contact for sufficient time, we recognize that the pressures of the two samples begin to change as indicated by the changes in their pressure gauges, and then equilibrate at some values, as indicated by no further changes in their respective pressures. When thermal equilibrium is achieved between the two samples the pressures will stabilize, and the pressure of the red sample drops while the pressure of the blue sample increases. Since volume and mass are kept constant, Gay-Lussac law tells us that the temperatures of the two objects must have changed. More precisely, the equilibrium pressure of the red object p_2 should be greater than p_4, so its temperature must have decreased from T_2 to T_3. Analogously, the pressure of the blue object should increase from p_1 to p_3, with an increase in its temperature from T_1 to T_3. Both objects must have the same temperature because their pressures do not change anymore, and therefore they achieved thermal equilibrium. Thus, when $T_2>T_1$, after equilibrium $p_3>p_1$ and both objects would have the same temperature, T_3. This is how we are going to test if a system achieved thermal equilibrium: by measuring changes in the pressures of the systems, when there are no further changes of the two objects in thermal contact, the two objects are in thermal equilibrium, and the two objects must have the same temperature.

7.2.2 The Statement of the Zeroth Law

Let's say that objects A and B are in thermal equilibrium. Let objects B and C be also in thermal equilibrium, separately. Then, we recognize that A and B have the same temperature and that B and C are also at the same temperature. Then, we arrive at the mathematical conclusion that A and C should also have the same temperature. Therefore, A and C must also be at thermal equilibrium.

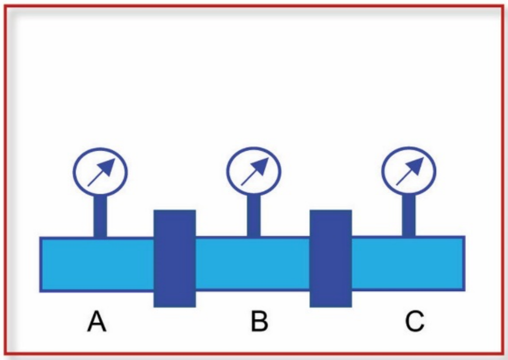

Figure 7.2 Thermal equilibrium between A and B, and between B and C proves that A and C are also at thermal equilibrium, and thus, A and C are at the same temperature. This is the fundamental principle (Zeroth law) used to measure the temperature of any object.

The situation is illustrated in Figure 7.2. The three gas samples A, B, and C are at different temperatures, initially, and then they are thermally connected and allowed to equilibrate. Each of these gas samples was fitted with a pressure gauge so that we can monitor the pressure changes and thereby changes in their temperatures. When A and B are brought to thermal equilibrium, then the two pressures will not change anymore over time. This way, we can deduce if A and B are in equilibrium or not and identify when they are equilibrated.

Now consider gas samples B and C that relate to a thermal bridge. When thermal equilibrium is established, their pressures will not change anymore as well. Therefore, we can also decide when B and C are equilibrated, and when there are no further changes in pressures, we may conclude that they are also in thermal equilibrium. Then, we recognize that B and C must have the same temperature.

Given the above two facts, Zeroth law states that if A and B are in thermal equilibrium, and B and C are in thermal equilibrium, then A and C must also be in thermal equilibrium. In simple terms, if the temperature of A is equal to the temperature of B, and the temperature of B is equal to the temperature of C, then the temperature of A must equal the temperature of C. This is a very simple, common sense mathematical conclusion, but important in determining the temperature of an object.

We will further analyze how this helps us in determining the temperature of the gas sample at hand. Consider a gas sample that is at zero degrees Centigrade, for example. We will use a gas thermometer to measure its temperature by the following method: A gas thermometer measures the pressure of the gas sample enclosed in it and from the pressure, we assess the temperature of the object of interest. We will discuss more these thermometers later. First, we equilibrate the thermometer with an ice bath (0˚C) until thermal equilibrium is achieved and then mark the pressure of the gas in the thermometer as 0 ˚C.

Now we take the thermometer and equilibrate it with the sample of interest, whose temperature is o ˚C, for the sake of argument. At thermal equilibrium, the gas pressure on the thermometer should read the same as the value obtained with the ice bath. This is because we intentionally kept the object at 0 ˚C. Then, we conclude that the ice bath and the object are at the same temperature, 0 ˚C. In doing so, we applied the zeroth law. Without the zeroth law, we will not be able to conclude that the ice bath and the object are at the same temperature. Thus, the zeroth law is essential for temperature measurements. If the object is kept at a different temperature, then our thermometer will read a different pressure than that obtained with the ice bath, and in that case, we would conclude that the object is not a 0 ˚C. In practice, this latter conclusion is not sufficient because we need to know what the exact temperature is, not just that it is not 0 ˚C. For this purpose, we will construct the thermometric equation as described below, using the zeroth law, for routine temperature measurements of different objects at various temperatures.

7.2.3 The Thermometric Equation

As described in the above experiment with the ice bath, we use a reference point and calibrate our thermometer to measure the temperature. We need at least two such reference points to construct a calibration curve. Also, we need to extend our approach to any thermometer, not just the gas thermometer, where we measured pressure as an indicator of temperature. We can choose any property of the substance to construct a thermometer if that property is a function of temperature. For example, the pressure and volume of a gas are functions of temperature and suitable for this purpose, but it could be the viscosity, electrical conductivity, resistivity, thermal expansion or thermal conductivity, or any other suitable property of the substance. The only stringent requirement is that it should vary with temperature, but it need not be a linear function. We will discuss this later point in more detail after we complete the derivation of the thermometric equation.

Having chosen a suitable property ‘y’ to construct our thermometer, we now proceed to calibrate. This we do with two reference points, the ice point, and the steam point. This reference state is readily produced by equilibrating ice-water mixtures at sea level (1 atm). The second reference state is the steam point where water is brought to boil at sea level (1 atm). We choose these reference points because they are conveniently produced in most laboratories. We can choose any reference point they want to if that state can be precisely reproduced in the lab or many labs. We measure the property ‘y’ at these two reference states, and we plot these two values as a function of temperature (t), as shown in Figure 7.3.

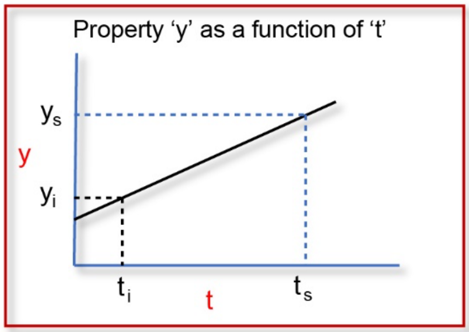

Figure 7.3 Plot of the values of the property ‘y’ as a function of temperature ‘t’ for the thermometer of choice. The values at the ice point and steam point are used to construct a calibration graph (straight line). Using this calibration line, we can measure any temperature ‘t’ by measuring the corresponding value ‘y’ with the thermometer. Only two calibration points are sufficient, which form a line.

The values of ‘y’ at the ice point and the steam point are joined by the calibration line, and we will examine the properties of this line and figure out how to measure the temperature of any object. The slope of the line is given by the first derivative of y wrt t and given as below.

$$\frac{dy}{dt} = \frac{(y_s - y_i)}{(t_s - t_i)}$$

In the above equation, y_s is the y-value at the steam point (t_s), y_i is the y-value at the ice point (t_i), The fraction on the right side of the above equation is simply obtained by writing the change in the y-value divided by the change in the t-value, as we normally define the slope of a line. We recognize that the plot will be linear because we only have two calibration points and therefore, the property ‘y’ varies linearly on this temperature scale. Thus, we need not choose a property that is a linear function of temperature, but we make it linearized on our scale of temperature. This is a very important detail, and it opens lots of possibilities to choose our thermometric property. Now, we rearrange the above equation to get the value of dy as below.

$$dy = \frac{(y_s - y_i)}{(t_s - t_i)}\, dt$$

By this equation, we have connected an infinitesimal change in y-value with the corresponding infinitesimal change in the t-value, and now we are ready to integrate this to obtain y as a function of t. Next, we need to choose a temperature scale of interest. To make things simple, we will choose the Centigrade scale as this is routinely used in science. Then, the temperature of the ice point is 0 ˚C, and that of the steam point, 100 ˚C. Our integrated equation should describe the change in y-values on a Centigrade scale. We integrate with an integration constant, C, as follows.

$$\int dy = \frac{(y_s - y_i)}{(t_s - t_i)} \int dt$$

$$y = \frac{(y_s - y_i)}{(100 - 0)}\, t + C$$

We evaluate C by substituting y = y_i when t = t_i and get the value C = y_i. The above linear equation is the thermometric equation on the Centigrade scale for any property y, which is a function of temperature, t. On this temperature scale, we forced y to be a linear function of temperature. We evaluate C by substituting y = y_i when t = t_i and get the value C = y_i and rearrange this to obtain ‘t’ instead of ‘y’, by the following two simple steps.

$$y = y_i + \frac{(y_s - y_i)}{100}\, t$$

$$\frac{(y - y_i)}{(y_s - y_i)}100 = t$$

If once we measure y_s and y_i values at the corresponding reference states, we simply measure 'y' at any temperature of the object of interest by equilibrating our thermometer with it. From the observed y-value, we then calculate the t-value of the object using the thermometric equation. This t-value will be in Centigrade due to the values we chose for the steam point and the ice point. Similarly, we can write thermometric equations for any temperature scale, and one of the most important ones is the absolute scale of temperature. The next section shows how we write the thermometric equation for the absolute scale of temperature.

7.2.4 Constant volume thermometer

Gases are the early substances to be used for temperature measurements, and we could use either volume of the gas or the pressure of the gas as the thermometric property. It is convenient to keep the volume constant and measure the pressure, and hence a constant volume, or pressure thermometer is chosen for constructing the absolute scale of temperature. We write the corresponding thermometric equation in terms of pressure (p) using the reference states, pressure at the ice point (p_i), and pressure at the steam point (p_s).

$$t = \frac{(p - p_i)}{(p_s - p_i)}100$$

This is our constant volume thermometer, where the pressure is changing but the volume is kept constant, and the mass is kept constant. Therefore, the pressure is a function of temperature or *vice versa*. We read out the pressure of the gas in the thermometer and from that, we calculate the temperature, t. This is the thermometer we used, implicitly, in the discussions of the zeroth law.

Example 7.1

Write a thermometric equation for a constant pressure thermometer and also for a thermometer that uses the length of a steel rod as the thermometric measurement.

The constant pressure thermometer measures change in the volume to determine the temperature. The corresponding thermometric equation is written easily by replacing the pressure terms with the corresponding volume terms, as follows. The V_s and V_i are the corresponding volumes at the steam point and the ice point, respectively.

$$t = \frac{(V - V_i)}{(V_s - V_i)}100$$

Similarly, the thermometer that uses the thermal expansion of a steel rod will have length (l) as the thermometric property and its thermometric equation is given below. The symbols l_s and l_i are the lengths of the steel rod at the steam point and the ice point, respectively.

$$t = \frac{(l - l_i)}{(l_s - l_i)}100$$

Pressure, however, of real gases is not a unique function of temperature. For example, if we fill our gas thermometer with nitrogen and make the measurement of temperature and then change the gas to oxygen, we will arrive at two different temperature values. This is because the pressure of nitrogen varies with temperature differently from that of oxygen to a certain extent. For example, the van der Waals constants a and b are different for different gases. This outcome is highly disconcerting because the measured temperature depends on the type of gas used in the pressure thermometer we constructed. This is analogous to rulers made of different materials, giving different lengths for the desk at the office. What is the true length of the desk?

This issue can be remedied by calibrating each thermometer independently, by measuring the pressures at the ice point and the steam point. However, this is cumbersome and still will not be satisfactory. There is a much more elegant solution to the issue. This solution also allows us to define the absolute scale of temperature, which is discussed below

7.2.5 Conversion of Fahrenheit to Centigrade

Historically, there has been several scales of temperature and Fahrenheit (˚F) is one of the popular ones in the US. The ice point on this scale is 32 ˚F and steam point is 212 ˚F. The conversion of the Fahrenheit to the Centigrade (˚C) is carried out by multiplying the value with 5/9 and adding 32.

$$t/{}^{\circ}C \ = t/{}^{\circ}F * (5/9) \ + 32$$

When the value of is very large, then the Centigrade scale is approximately one half.

Example 7.2

For college admission, I was asked this question. At what temperature do the values of Centigrade and Fahrenheit are equal?

Using x ˚C for Centigrade and x ˚F in the conversion equation, and then solving for x, we get x=-40.

$$x/{}^{\circ}C \ = x/{}^{\circ}F * (5/9) \ + 32$$

At this temperature, both thermometers read exactly the same temperature!

7.3 Absolute scale of temperature

Our gas thermometer readings will change from gas to gas used to construct it, the temperature measured would depend on which type of gas we have used, and that's a fundamental problem addressed by Lord Kelvin. The following amends this problem and leads to the absolute scale of temperature. The thermometric equation written for the Centigrade scale, for the constant volume thermometer, is given below. We separate the two terms in the numerator by writing two separate fractions.

$$t = \frac{(p - p_i)}{(p_s - p_i)} 100 = \frac{100\ p}{(p_s - p_i)} - \frac{100\ p_i}{(p_s - p_i)}$$

When the pressure of the gas at the ice point is infinitesimally small, near zero, then an interesting limiting condition is obtained. Lord Kelvin defined this limiting value as T_o, and experiments indicate that this is a constant (273.15). That is, it is independent of the gas used in the thermometer.

$$T_o = \lim_{p_i \to o} \frac{100\ p_i}{(p_s - p_i)} = 273.15$$

By re-writing the above thermometric equation using this constant for the second fraction, we get the equation below, at p_i approaching zero.

$$t = \frac{100\ p}{(p_s - p_i)} - 273.15$$

Now, define the kelvin scale of temperature (T) using this constant, and this is the absolute scale or the thermodynamic scale of temperature (K). Note that the pressure p is used here to obtain the temperature T, different from ‘t’. The two temperature scales differ by a constant of 273.15.

$$T = \lim_{p_i \to o} \frac{100\ p}{(p_s - p_i)}$$

This is the absolute scale of temperature. When the limiting condition that the pressure of any gas in the thermometer at the ice point be vanishingly small is obeyed, the constant turns out to be 273.15 irrespective of the gas used. Thus, we can use any gas in our thermometer to make the temperature measurements. This limiting condition is explicitly indicated in the above equation and should be kept in mind in constructing our gas thermometer.

7.3.1 Absolute low limit for temperature for anywhere in the universe

Note the important point that T = 0 at -273.15 ˚C from the above equation, and from Charles’ law we learned that we can’t reach this temperature, which has been experimentally proven. By extending the plot, we recognize that a temperature below 0 K implies that the gas volume be negative, which is not possible (Figure 7.4).

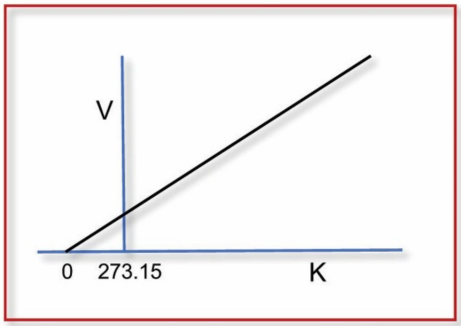

Figure 7.4 Linear plot of volume vs T (K) for a constant pressure thermometer suggesting the absolute lower limit for temperature in the universe.

Thus, we conclude that achieving absolute zero is not possible. When we set the pressure approaching zero atm at the ice point for our thermometer, we are invoking nearly ideal behavior and hence, all gases will tend to give the same temperature reading on the thermometer. At this limit of low pressure, the percent increase in pressure at the steam point is a constant for all gases and equals 273.15. This observation led to the construction of the thermodynamic scale of temperature. The ° symbol is not used on the kelvin scale because the kelvin scale is not relative but an absolute scale. This aspect is taken into consideration in the construction of the absolute scale of temperature. The exact value of kelvin is to be changed slightly in 2019 to get the exact value for the Boltzmann's constant.

It is predicted that 0 K is the absolute lower limit of temperature anywhere in the universe, a very powerful conclusion. This is extraordinary and why thermodynamics is powerful and controls the universe at many levels. The lowest temperature achieved so far is 100 pK.[26] We will see this power of thermodynamics in other chapters of this book as well.

7.4 Molecular interpretation

The zeroth law is a fundamental law governing the measurement of temperature, and it allows quantitative measurements of temperature. At the molecular level, the exchange of kinetic energy among the particles of the two objects in thermal equilibrium results in the equalization of their temperatures. When the net exchange of kinetic energy among the objects is constant, equilibrium is achieved and hence, the two objects are at the same temperature. At absolute zero, the thermodynamic motion of the gas particles is predicted to cease, and hence, a lower temperature than 0 K can't be achieved because energy can't be <0. Quantum mechanics, however, predicts that all motion does not cease even at a 0 K. This is called the zero-point energy. Regardless, the lowest temperatures reached so far is ~100 pK but progress is still being made but no one has achieved negative kelvin temperature. If the temperature is negative, then KE is negative, which is possible only when velocity is imaginary. Thus, we can never achieve negative temperature but achieving even 0 K is not possible.

7.5 Applications in daily Life

The measurement of the temperature is an everyday experience and hence, we depend on the zeroth law for this purpose. Without the validity of this law, weather forecasting is not possible, as one example of numerous instances of temperature measurements. Just too numerous and abundant to mention here.

Kelvin scale of the temperature is used as the color the temperature for grading the color of light emitted by light bulbs and LEDs. The higher the color temperature, the bluer is the color of the light emitted. The lower the color the temperature, the warmer the color (more reddish) is. This is based on the black body radiator, which is discussed under the Quantum Chemistry topics.

7.6 Key points

1. Thermal equilibrium is established between two gas samples when their pressures do not change with time at constant volume and mass. This is a convenient method to determine the establishment of the thermal equilibrium between the two samples.
2. By limiting the pressure of the constant volume thermometer at the ice point to be vanishingly small, we invoke ideal gas behavior. Because of this condition, the percent change in the pressure at the

steam point is constant for all gases and has a value of 273.15. Thus, the addition of this constant to the Centigrade value gives us the thermodynamic scale of the temperature.

3. The thermodynamic (kelvin) scale of the temperature is defined as 273.15 K (corrected recently to 273.16) at triple point of water (0.1 ˚C). This value will be adjusted again in 2019.
4. The lowest temperature achievable in the universe is 0 K and nothing can be cooler than this!
5. The temperature on the Centigrade and Fahrenheit scales are indicated as a degree but this is not the case for kelvin scale, because the latter is the absolute scale and not relative like the others.
6. The precise definition of kelvin has been changed at the end of 2018 to create a finite value for Boltzmann's constant. But still, the freezing point of water is the same.

7.7 New Terms and Units

$$t = \frac{(p - p_i)}{(p_s - p_i)}100 \qquad t = \frac{(V - V_i)}{(V_s - V_i)}100 \qquad T = \lim_{p_i \to o} \frac{100\ p}{(p_s - p_i)} \qquad T_o = \lim_{p_i \to o} \frac{100\ p_i}{(p_s - p_i)} = 273.15$$

Thermal equilibrium, Thermometric property, Thermometric equation, Thermodynamic scale of the temperature, kelvin (K), Centigrade (˚C), Fahrenheit (˚F), absolute zero K temperature**.** Units of temperature are ˚C on the Centigrade, ˚F on Fahrenheit and K on the kelvin scale. The degree symbol is not used on the absolute scale, because it is not a relative scale.

7.8 Self Reflection

1. Construct a personal scale of the temperature (˚i) using steam point and ice point as 200 and 0 ˚i, respectively. How is that related to the Centigrade scale?
2. Consider the space of your dorm room and design an experiment to calibrate a new thermometer.
3. Consider the space of your car and give instances where you could use a good thermometer.
4. Imagine you are hiking through a desert, and you needed a thermometer to measure how hot it is. How would you make a make-shift thermometer when all you have is a rubber balloon, a ruler, a basic calculator, and an equation sheet from this course?
5. In the above problem, what if you have a melting ice pack, empty water bottle, clear plastic tube, and a fire starter kit, instead?
6. Plot V vs T at constant the pressure and mass for an ideal gas, on the absolute scale of the temperature.

7.9 Further Reading

1. Physical Chemistry by Castellan, 3rd Edition 1967
2. https://ocw.mit.edu/courses/chemistry/5-60-thermodynamics-kinetics-spring-2008/video-lectures/lecture-1-state-of-a-system-0th-law-equation-of-state/

7.10 Self Tests

1. According to the Zeroth Law, if A and B are in thermal equilibrium, and B and C are in thermal equilibrium then A and C

a. should have different temperatures

b. are at the same height

c. are at the same pressure

d. should have the same temperature

e. none of these

Use the following volume vs. temperature plot of gases for questions 2-5.

2. Temperature lower than 0 K is not possible because it would imply:

a. infinite volume

b. infinite pressure

c. negative volume

d. the zeroth law of thermodynamics is not valid

e. none of these

3. What is the predicted absolute lower limit of temperature for anywhere in the universe?

a. 0 K
b. -1000 K
c. -273.15 ˚C
d. both a and c
e. none of these

4. As temperature increases, the volume of the gas ________.

a. decreases
b. increases
c. remains the same
d. unpredictable
e. none of these

5. The triple point of water is defined at

a. 273.15 K
b. 273.15 ˚C
c. 0 K
d. none of the above
e. 300 K

6. What is lower than the lowest temperature ever achieved as of 2018?

a. -90 pK
b. 100 pK
c. -250 ˚C
d. -250 ˚F

7. The unit for the absolute scale of temperature is

a. ˚C
b. ˚F
c. ˚K
d. K
e. none of these

8. Under what conditions, thermal equilibrium is established between two gas samples, when their pressures do not change with time?

a. volume and mass
b. pressure and temperature
c. constant mass
d. constant temperature
e. none of these

9. Which of the following is the thermodynamic scale of temperature?
   a. Celsius
   b. Fahrenheit
   c. Kelvin
   d. Boltzmann
   e. none of the above

10. What is a steam point of water?
   a. 100 ˚C
   b. 0 ˚C
   c. 0 ˚K
   d. 0 K
   d. none of the above

11. Which of the following is the thermometric equation?
   a. $\frac{dy}{dt} = \frac{(y_s - y_i)}{(t_s - t_i)}$
   b. $dy = \frac{(y_s - y_i)}{(t_s - t_i)}\, dt$
   c. $y = \frac{(y_s - y_i)}{(100 - 0)}\, t + C$
   d. $y = y_i + \frac{(y_s - y_i)}{100}\, t$
   e. all the above

12. Which of the following is the thermometric equation for a constant pressure thermometer?
   a. $\frac{dy}{dt} = \frac{(y_s - y_i)}{(t_s - t_i)}$
   b. $dy = \frac{(y_s - y_i)}{(t_s - t_i)}\, dt$
   c. $t = \frac{(p - p_i)}{(p_s - p_i)} 100$
   d. $t = \frac{(V - V)}{(V_s - V_i)} 100$
   e. all the above

13. Which of the following is the equation for the absolute scale of temperature?
   a. $T = \lim\limits_{p_i \to o} \frac{100\ p}{(p_s - p_i)}$
   b. $dy = \frac{(y_s - y_i)}{(t_s - t_i)}\, dt$
   c. $t = \frac{(p - p_i)}{(p_s - p_i)} 100$
   d. $t = \frac{(V - V)}{(V_s - V_i)} 100$
   e. none of the above

14. Which of the following is the equation for the constant volume thermometer?

a. $T = \lim\limits_{p_i \to o} \frac{100\ p}{(p_s - p_i)}$

b. $dy = \frac{(y_s - y_i)}{(t_s - t_i)}\ dt$

c. $t = \frac{(p - p_i)}{(p_s - p_i)} 100$

d. $t = \frac{(V - V)}{(V_s - V_i)} 100$

e. none of the above

15. Which of the following is the equation for the Centigrade scale?

a. $T = \lim\limits_{p_i \to o} \frac{100\ p}{(p_s - p_i)}$

b. $dy = \frac{(y_s - y_i)}{(t_s - t_i)}\ dt$

c. $t = \frac{(p - p_i)}{(p_s - p_i)} 100$

d. $t = \frac{(V - V)}{(V_s - V_i)} 100$

e. all of the above

16. The zeroth law is important for the measurement of what?

a. pressure

b. volume

c. temperature

d. mass

e. none of these

17. What temperature scale is usually specified for the color temperature of light bulbs or LEDs?

a. Centigrade

b. Fahrenheit

c. Kelvin

d. arbitrary scale

e. none of these

18. At what temperature is the thermodynamic motion of gas particles is predicted to cease?

a. 100 K

b. 100 ˚C

c. 0 ˚C

d. 0 ˚K

e. 0 K

19. What is the approximate temperature produced by the large Hadron collider in Switzerland?

a. several thousand ˚C

b. several million ˚C

c. several million K

d. several billion ˚C

e. none of the above

20. What is the nearest value of the limit $T_o = \lim_{p_i \to o} \frac{100\, p_i}{(p_s - p_i)}$

a. 0 ˚C

b. 273.15 K

c. 273 ˚C

d. 273

e. none of the above

7.11 Self Tests Key

1. d, 2. c, 3. d, 4. b, 5. a, 6. b, 7. c, 8. a, 9. c, 10. a, 11. d, 12. d, 13. a, 14. c, 15. e, 16. c, 17. c, 18. e, 19. d, 20. e.

7.12 Problems

1. What is the temperature in ˚F that corresponds to 37 ˚C? (Ans. 98.6 ˚F)
2. What is the room temperature (25 ˚C) on the Fahrenheit scale? (Ans. 45.9 ˚F)
3. The volume of a constant mass of an ideal gas changes from 1 L to 1.5 L on heating under constant pressure conditions from an initial temperature of 25 ˚C. What is its final temperature in K? (Ans. 447.2 K)
4. In a constant volume ideal gas thermometer containing 0.01 mol of gas in 10 mL bulb, the pressure was increased by 10 Torr when the temperature was increased. What is the change in the temperature on the kelvin scale? (Ans. 0.16 K)
5. Old medical thermometers used 0.61 g of mercury in their bulb. If the capillary of the thermometer connected to the bulb has a diameter of 0.1 mm, what is the change in the height of the mercury thread in the capillary per 1 ˚F? (Ans. 0.14 mm)
6. The railroad tracks are made of steel with a linear coefficient of expansion of 0.0000065/˚F) and expand on heating during a summer day. If the temperature variation in the location over a year is as much as 120 ˚F, what should be the gap between rails of 100 m long, in cm, such that the tracks stay flat at either extreme temperature and not buckle? (Ans. 7.8 cm)

Chapter 8. Thermodynamic Paths and Processes

After completing this chapter, you will be able to:

- Identify thermodynamic terms and recognize their meaning and context of the application.
- Recognize the definitions of state, system, surroundings, universe, path, process, and other important thermodynamic terms.

Goal

- Define the system, surroundings, boundary, path, initial and final states, process, heat, and work.
- Apply these terms in the analysis of the thermodynamics of chemical reactions and physical processes.

8.1 Why Study this?

In this chapter, we will discuss definitions of a variety of variables and attributes that we use in chemical thermodynamics, and we need to be clear about these words and their precise meaning. We need to master these terms to fully analyze the thermodynamics of chemical reactions or physical processes. Thus, without this terminology, we will not be able to apply thermodynamics at all. Just as learning the alphabet of a language is essential to learn to write in that language, these terms are our alphabets of thermodynamics and essential to our study. Rules of grammar for this thermodynamic language, analogously, will follow in the later chapters.

We will define and discuss processes including the processes that occur spontaneously or naturally. Spontaneous processes are important to us because if a chemical reaction is designed to be a natural process, then it will occur spontaneously making the life of a chemist easier. Thus, a fundamental understanding of what makes a process spontaneous is of paramount importance. Along these lines, we will examine cyclic processes, reversible processes, and irreversible processes. These details will lead us into the investigations of the first law of thermodynamics in a later chapter.

8.2 System and surroundings

One of the most important words to recognize in our alphabet is the system. The other two terms are the boundary and surroundings. While we are free to choose these as we desire for the experiment at hand, we will have to fully recognize their meaning, differences, limitations, and similarities. Attention to this section of the chapter is quite important.

8.2.1 System

The system is simply the region of the universe that is of immediate interest to us. We can examine the changes that are happening or happened within the physical limits of the space defined as the system. This kind of definition sounds very vague but it implies that we can choose the system in any way we desire and define it as we like. But once we choose our system, and as part of the universe, we will have to pay close attention to its contents, attributes, and limits. We define the system depending on what we want to accomplish. For example, we can define a cup of coffee as including the cup and the vapors above the liquid. Or we can define it as the coffee liquid only and exclude all other parts from it. We have the freedom to choose the system of interest as part of the universe, but this is by no means a random act. We must keep in mind our goals for the analysis of the system and choose it appropriately. Usually, we define the system by enclosing the space of interest by a real or an imaginary surface. This surface is the boundary that separates the system from the rest of the universe. For example, the coffee cup and the surface of the liquid on the top can form the boundary of the liquid if we choose the liquid enclosed by these boundaries as our system. We identify the system by precisely defining its boundary, as completely as possible. By defining the system, we should be able to delineate everything inside (Figure 8.1).

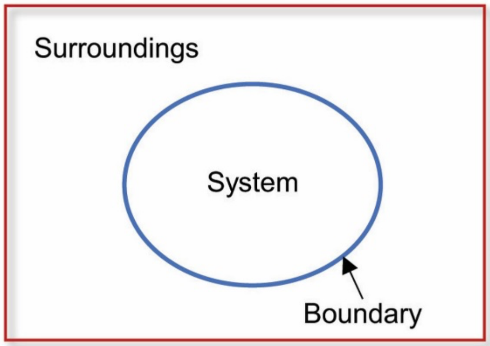

Figure 8.1 The system, boundary, surroundings, and the universe are illustrated here.

8.2.2 Surroundings

Everything outside of our boundary of the system is defined as the surroundings. We distinguish the system from its surroundings by the boundary. Surroundings are that part of the universe which do not belong to the system, and so we have only two things -- system and surroundings -- nothing else. The boundary separates the surroundings from the system (Figure 8.1). Then, by extension, the system plus surroundings is the universe, because everything other than the system in the universe is the surroundings. This generalized but specific definition of the surroundings is important. Everything must belong to either the system or the surroundings, nothing else, and everything belongs to the universe.

The red rectangle, let us say, represents the entire universe we live in (Figure 8.1) and the blue oval represents the space that we define as our system with whatever is inside that oval shape. Everything outside the blue oval are the surroundings, and the blue border separating the system from the surroundings is our boundary. Therefore, we recognize the system and its surroundings, but we need to recognize different kinds of systems as described below.

8.2.3 Open System

Consider a beaker of water as our system with the boundary enclosing the entire mass of water, at the beaker walls, bottom, and the liquid-air interface. This system is open to the atmosphere and so the water vapor can leave the beaker and escape into the surroundings, the atmosphere. The system can lose some of its mass or we can add some back, and so it can exchange mass from the surroundings. If we heat the beaker on a burner, the temperature of the water can increase, and we can exchange energy with the surroundings. A system that can exchange both mass and energy with the surroundings is called an open system (Figure 8.2A). We could also put an air-tight lid on top and redefine the system as the entire beaker with the lid, then it is no longer an open system because it can't exchange mass with the surroundings. We need to be careful in defining the system as completely as possible and recognize that an open system can exchange both mass and energy with its surroundings.

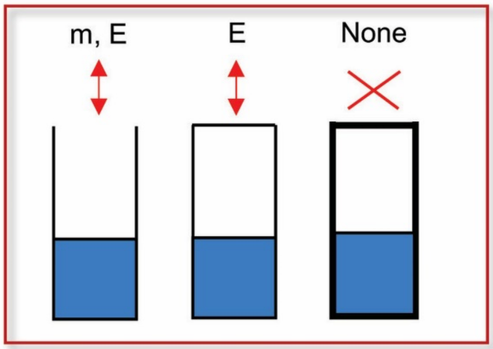

Figure 8.2 The open (left), closed (middle), and isolated (right) systems.

8.2.4 Closed System

In contrast to the above case of an open system, we can choose to prevent the exchange of mass by placing an air-tight lid on the beaker, so that water vapor can't escape into the atmosphere above it (Figure 8.2B). However, the walls of the container or the lid may receive heat or exchange heat with the surroundings. This kind of system that can exchange energy but not mass with its surroundings is termed the closed system. It is closed to the exchange of mass but not energy (Figure 8.2B). A constant volume calorimeter or the closed reaction vessel of an organic chemistry synthesis pot are examples of closed systems. We often encounter closed systems in the lab unless we allow the exchange of mass. Our planet earth may be considered as a closed system because it can readily exchange energy with its surroundings, like the sunshine, but essentially it does not exchange mass. Unless, of course, when a meteor lands on the planet or when a spacecraft leaps into space.

8.2.5 Isolated System

When our system can neither exchange energy nor mass, then we call it an isolated system (Figure 8.2C). There are no true isolated systems in the lab because we may be able to prevent the exchange of mass but preventing the exchange of energy is difficult. A beaker of water, a cup of coffee, a round bottom flask with chemicals, etc., are all examples that can exchange energy, but we can allow or disallow the exchange of mass. Even when we insulate the system it can still exchange some energy at a certain rate.

There is, however, only one example of a truly isolated system -- the Universe. The physical universe itself is a system that we can define. Since the universe is everything that practically exists, it has no surroundings and hence neither energy nor mass can enter or leave from/to its non-existing surroundings. Thus, the universe is the only true isolated system, and we will consider it in one of the next chapters of this book.

Example 8.1

It seems to be impossible to prevent the exchange of energy. Even a nearly perfect thermos flask leaks some energy in or out. Therefore, there may be no isolated systems, but we approximate such systems by insulating them heavily and closing off all energy/mass exchanges with its surroundings, for all practical purposes. A good constant volume calorimeter will come close to being an isolated system when it is operating well.

8.2.6 State of the system

Another important step is to define the state of our system, which means defining all its attributes such as its boundary, its properties such as mass, volume, pressure, temperature, and other variables that we care about. When all these attributes are defined, then we have defined the state of the system. We normally recognize the variables: amount (mole numbers, number of chemical/physical species present), pressure, composition, volume, and temperature. We define the state of the system as completely as possible by identifying values for such variables as best as we can and as many as we need. This state will also be the initial state of our system.

8.2.7 Change, the initial state, and the final state

Any alteration in the attributes of our system in the initial state constitutes a change. For example, the pressure may change due to a reaction or acceptance of energy from the surroundings, and then we announce that the system has changed from an initial state to a final state with this change in the pressure. Any change in the property of the system induces a change in the state of the system. When the system undergoes a change, then it has traveled from an initial state to a final state, and we precisely define the attributes of the system in its initial state as well as the final state, and we report that a change has occurred in one or more properties of the system.

One powerful convention that we will follow throughout our discussions is how we report a change. We always report the change in any property of a system as the value of the property in the final state minus its value in the initial state. That is, change in state is represented by the prefix 'Δ' (delta) and it is always the value of the property in the final state minus the value of the property in the initial state.

Example 8.2

Two examples will be given to clarify the above point, the changes in pressure and temperature. The change in the pressure is given as 'Δp' and it is the pressure of the final state (p_{final}) less the pressure of the initial state ($p_{initial}$).

$$\Delta p = (p_{final} - p_{initial})$$

Similarly, we can write change in the temperature of the system as the difference between the final and initial temperatures of the system as the temperature change occurs in the system.

$$\Delta T = (T_{final} - T_{initial})$$

8.3 Path

When a change occurs in a system, it moves from an initial state to a final state (Figure 8.3). The series of intermediary steps that the system travels from the initial state to the final state is the path the system has traveled. Certain changes in the system have displaced it from the initial state (pink oval) to the final state (blue oval). We can connect the initial and final states via distinct intermediary states, and we can have a curved path (1) or a straight path (2) or a wavy path (3), or any other path. There could be infinite different routes through which the initial state could travel to produce the final state. It is like traveling from Storrs CT (initial state) to Hartford CT (final state) and one can take so many different roads in different combinations to reach the destination. Then, whenever there is a change in a system, we have a path that connects the initial state with the final state.

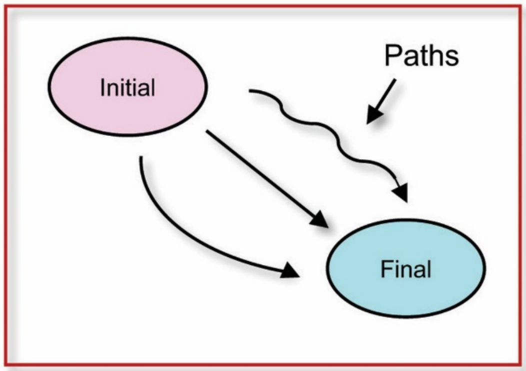

Figure 8.3 Path connecting the initial and final states represents a series of the intermediary states and there can be many different paths (curved, straight, and wavy lines) that can potentially connect a given set of initial and final states. Specification of the path is important for certain functions, called path functions, while the specification of the path is irrelevant for assessing the changes in the state functions, which do not depend on the path traversed.

8.3.1 Path functions

There are two kinds of thermodynamics functions for our analysis: those that depend on the path and those that do not depend on the path. When a system travels from an initial state to a final state, it may have gone through a particular path. Some properties of the system are intimately connected with the path, and the changes in their values depend on the path traversed, and these are the path functions. In other words, these functions not only depend on the initial and final states of the system, but also on the path that the system has traveled. Mathematically, these functions do not produce exact differentials. Since their values depend on the path, we do not write them in a standard differential form and the corresponding integrals depend on the path.

Example 8.3

Two important properties what we care in this course that are path functions are heat and work. We will show later that these are path functions, and we can't write exact differentials of these quantities. However, we make these state functions by defining the path. Thus, heat capacity at constant volume, for example is a state function but not a path function.

8.3.2 State functions

On the other hand, there are characteristic functions of our system that do not depend on the path but depend only on the initial and final states of the system. These are called state functions. We can write exact differentials of these functions and we can integrate them by the standard methods of calculus. We often write infinitesimal changes in the properties of the state functions by the standard differential operator and integrate these functions. In addition, there are several other interesting properties of the state functions which we will use in the subsequent chapters. We will soon recognize that energy, enthalpy, entropy, and many other properties are state functions and the changes in their values accompanying the travel of our system do not depend on the path. Next, we examine heat and work and their operational definitions.

Example 8.4

Define the path, surroundings, system, and change, when we make a cup of coffee in the morning. Use your imagination to choose the system appropriately.

We define the coffee cup with liquid water filled two-thirds the way with the boundary of the liquid separating the surroundings from the system. We choose this as an open system so that we can add the coffee powder, milk, and sugar to taste. We heat the coffee in the microwave and transfer some energy from the surroundings into the system. As we sip the coffee, the mass is being moved out of the system and into the surroundings. Thus, the open system is a good choice for this example. When we leave it on the table, we find that some heat energy is dissipated across the boundary into the surroundings, and then the temperature of the coffee decreases with passing time, open system, and hence, it is advisable to drink it sooner than later to enjoy the cup of joe.

8.4 Processes

A process is a specific set of conditions under which certain changes occur in our system as it travels along a path from the initial state to the final state. Certain properties of the system may be pre-defined to be kept constant during the process. This allows for appropriate differentiation of the functions of interest for a given set of processes under these conditions. For example, Boyle’s law is carried out under constant temperature conditions, and we call that an isothermal process, as explained below.

8.4.1 Isothermal process

An isothermal process is a process where the temperature of the system is kept constant, throughout the travel of our system, along the path from the initial state to the final state. All other properties may be allowed to change except the temperature during the isothermal process. Keep in mind that during an isothermal process, we may add or remove heat from the system to keep the temperature constant. Boyle’s law is an example of the isothermal process we encountered in an earlier chapter. Another important process that we are concerned about is the adiabatic process.

8.4.2 Adiabatic process

An adiabatic process is one when no heat appears at the boundary of the system during the change from the initial state to the final state. To prevent heat from entering or leaving the system, we insulate the system from the surroundings as best as we can, and the system can be closed or isolated. Just because $q = 0$ during an adiabatic process does not mean that the temperature of the system remains the same, this will be addressed after the first law is discussed. Two other processes that we are concerned about will be the isobaric and isochoric processes, which are discussed below.

8.4.3 Isobaric and isochoric processes

Isobaric, means constant pressure, and the isobaric process is one during which the system travels from the initial state to the final state along a path where the pressure is kept constant at every intermediary step. For example, Charles’ law is an isobaric process where we vary the temperature and examine the volume of the gas, at constant p and mass. The isochoric process is one where the volume is kept constant as the system travels from the initial state to the final state. An example of the isochoric process is the Gay-Lussac law, where we examine the pressure as a function of the temperature while keeping the volume and mass constant. Thus, we can impose certain restrictions on a process, and we need to keep this in mind while writing the differential expressions for the state or path functions. The next item that we are concerned about is the cyclic process.

8.4.4 Cyclic process

A cyclic process is one during which the system travels through a path and returns back to its exact initial state (Figure 8.4). We pass through intermediary states 1-3, for example, and reach the initial state. Thus, the path is cyclic, the system need not travel back on the same path, and the path can be unique. For example, you fly from New York City to Los Angeles direct, and on the way back you travel to Chicago, then to Hartford, and back to New York City. This is an example of a cyclic process, and our system can similarly make stops at certain points and end up at the initial state. This is a cyclic process because the initial state has been regenerated through the process. One could fly a round trip from New York City to Los Angeles and back, and that also is a cyclic process. So far, we have focused on the system and not paid any attention to what is happening in the surroundings. Based on what is happening in the surroundings, we have two distinct types of processes, the corresponding cyclic processes as discussed below.

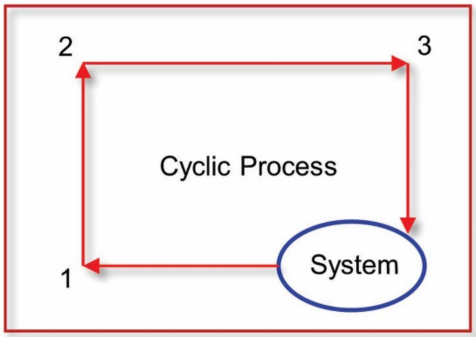

Figure 8.4 Cyclic process involves a path with states 1, 2, 3 that ultimately lead to the same exact initial state. Note that the system may travel along various paths. Also, note that we do not specify what is happening to the surroundings. This is intentional and more details are provided later.

8.4.5 Irreversible processes

An irreversible process, by definition, is not a reversible process (Figure 8.5). That is when the process is reversed, either the system or the surroundings are not returned to their initial state. For example, consider the green oval in Figure 8.5 as the system or the surroundings, and the forward process may convert it to the blue rectangle. Upon reversal of the forward process, one possibility is that the green oval is reproduced, and then the process is reversible. The other possibility is that, upon reversal of the process, one obtains the unfilled rectangle, which is not the original system or the surroundings. When the system and the surroundings are not restored, we have an irreversible process. There are lots of irreversible processes in nature that we see. Let's take an example to clarify what an irreversible process is.

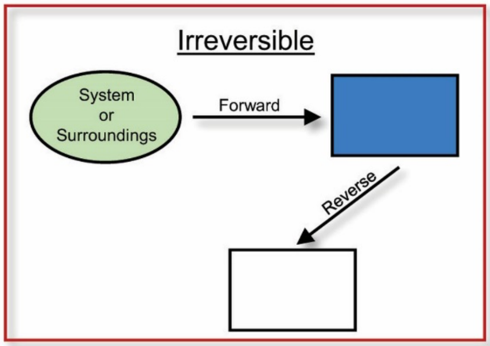

Figure 8.5 A process is irreversible when either the system or the surroundings can’t be restored to their initial state when the process under investigation is reversed. Falling apple is a typical irreversible process.

Example 8.5

Consider a large stone that is on the top of the hill, and it rolls down the hill spontaneously into the valley. The stone rolls down the valley by itself, a natural process, and reaches the valley floor (Figure 8.6). Define what is our system, what is the boundary, path, and what are the surroundings? Let us say, for the sake of argument, we define the stone as our system, the surface of the stone as the boundary, and everything else, the surroundings. When the stone is at the top of the hill before rolling down, it is in its initial state, and when it reached the floor of the valley it is in its final state. It travels a path on the surface of the hill, under the influence of the field of gravity, from its initial state to the final state.

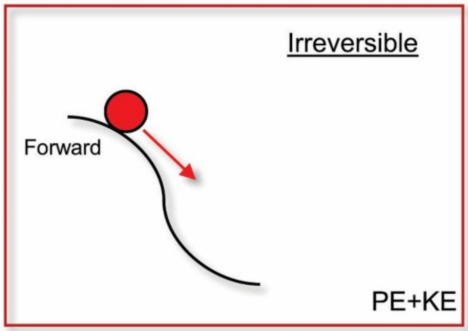

Figure 8.6 Falling of a stone down the hill is an irreversible process, even if we lift the stone back to the top of the mountain and restore its initial state. This is because certain parts of the surroundings are not restored to their original state even when we push the stone up the hill. Thus, there have been some permanent changes in the surroundings when the process is reversed, making it an irreversible process.

Example 8.6

Analyze the forward process of falling of the stone in the above example is a reversible or irreversible process.

As the stone rolls down the hill, it bumps and dings into rocks and soil and plants and whatnot, and releases some of its kinetic energy as thermal energy into the surroundings through the boundary. Due to these impacts, some heat may have been dissipated into the surroundings and some stones may have been scattered up, doing work in the surroundings. Finally, it comes to rest on the valley floor. Then, maybe the stone is warmed due to the friction and grinding, and then it cools and reaches the final state. During the forward process, the potential energy of the stone is being converted to kinetic energy, and some of that kinetic energy is converted into other forms of energy as it travels down the slope, until the stone comes to rest at the bottom of the valley. The kinetic energy that has been released into the surroundings is converted into heat/work and dispersed. This is our forward process, and it is an irreversible process.

Example 8.7

Analyze the above example, further, and indicate if the fall is a reversible or an irreversible process.

In the reverse process, we can carry the stone from the bottom of the hill and put it on the top, but this does not reverse all the processes that occurred during the forward process. That is, we need to convert any work done during the forward process on its way back to its potential energy and collect all the heat released during the fall back to its potential energy. Simply bringing the stone back to the mountain top leaves the changes in the surroundings permanent. This is simply because some changes in the surroundings have not been completely reversed during the reverse process.

We can certainly restore the system to its initial state, at least in principle, restore to the initial height, the pressure, the temperature, the volume, mass, *et cetera*. Still, it is not a reversible process unless we can also restore the surroundings back to their initial state. During the forward process, some of the kinetic energy of the system may have been transferred to stones, plants, dirt, and other objects in the surroundings, and this might have raised their temperature and/or height, may have broken some twigs, crushed some bugs, or broken some branches, etc., Thus, during the forward process, some of the potential energy of the system has been transferred into kinetic energy and has been dispersed into the surroundings. So, the process can be made reversible only if we collect all this energy from the surroundings and put it back into the system as potential energy. That is, all the energy that has been dissipated should be collected and utilized to propel the rock up the hill to its initial position. This is not happening when we lift the stone back to its initial state, and we have no way of reversing all the events that have occurred in the forward process. Thus, the surroundings would have undergone permanent changes, and because the surroundings suffered a permanent change, this is an irreversible process. In fact, all the natural processes that are happening around us in the universe, are irreversible. They leave certain permanent changes in the system or the surroundings as they happen. Next, we will examine what a natural process is, for a better handle on these details.

Example 8.8

Examine closely if making a cup of coffee in the morning or evening is a reversible or irreversible process. Use your imagination to choose the system appropriately.

We define the coffee cup with liquid water filled two-thirds the way, with the boundary of the liquid separating the surroundings from the system. We choose this as an open system so that we can add the coffee powder, milk, and sugar to taste. We heat the coffee in the microwave and transfer some energy from the surroundings into the system. This is an irreversible process because some masses are lowered in the surroundings and by restoring them to their original place, the cup of water will not emit microwaves, and the microwave generator does not run backward to produce current. As we sip the coffee, the mass is being moved out of the system and into the surroundings and certainly, this occurs abruptly and requires biological work to be performed. By transferring the coffee back into the cup does not run these biochemical reactions in the reverse direction. Thus, this is another irreversible step. When we leave the cup on the table, we find that some heat energy is dissipated across the boundary into the surroundings, and coffee temperature decreases with time. Hence, it is also an irreversible step, and this last step will be discussed further in the upcoming chapters.

8.4.6 Natural processes

The leaf (our system) falling from the tree to the ground, in the Fall season in New England, is a common observation and this happens all by itself, no one needs to detach the leaf from the tree and push it down. Therefore, it is a natural process, which occurs all by itself. If we mix sodium metal with chlorine gas, it ignites immediately, in an explosive reaction. This is a natural process. Thus, we witness processes taking place all around us, all occurring without our assistance, all by themselves.

Example 8.9

Analyze the reverse and forward processes of falling leaf.

We never see the leaf flying back up and attaching itself to the tree stem. This is not a natural process. Thus, the forward process is a natural process, and the reverse is not. As the leaf detaches itself from the stem automatically, due to the action of certain enzymes that degrade the tissue in the stem to allow it to weaken, and leaf travels through the air, it is warmed due to friction with the atmosphere, ever so slightly. When it finally hits the floor or the soil and lands, it comes to rest. When it comes to rest, its kinetic energy is converted into thermal energy and dissipated into the surroundings. We readily conclude that this must be an irreversible process because we can’t collect all the energy dissipated into the surroundings during the forward process and use it to attach the leaf back to the tree and restore the initial state of the system as well as the surroundings.

Thus, we can look at several different natural processes that are taking place in the universe. We are particularly interested in these because if we can make our chemical reaction of interest into a natural process, we can just watch it happen! No need to put effort into making it happen. The thermodynamics of natural processes or irreversible processes is of high interest to chemists, and similar applications of natural processes can be found in all other disciplines of science as well.

8.4.7 Reversible processes

A reversible process is one where the system travels a specific path to reach the final state during which the surroundings have undergone certain changes, but when the entire process is reversed, both the system and the surroundings are restored to their respective, exact initial states (Figure 8.7).

We start with the system (blue circle) and the surroundings (purple square) in their respective initial states, and we reach a final state where the system has undergone some change (red oval). There has been a corresponding change in the surroundings as well (blue rectangle). When we reverse the process, the system in the final state (red oval) turns into the blue circle (initial state), while the surroundings are also restored back to their initial state (purple square). The only difference between the forward and the reverse paths is the direction. Thus, there are no net changes, either in the system or in the surroundings, when the forward process is reversed. This is thermodynamic reversibility, and it is quite different from what we generally consider as reversible. The corresponding cyclic process (forward + reverse) is also reversible, and it is a reversible cyclic process.

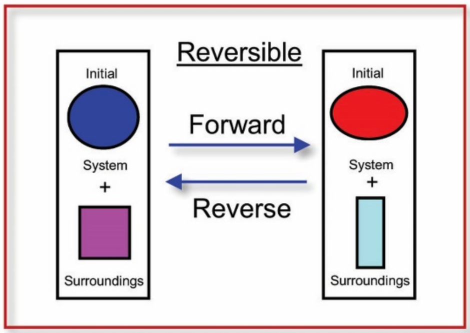

Figure 8.7 Reversible process is defined as a process where the system and surroundings undergo a change during the forward process but when the process is reversed, both the system and the surroundings are completely restored to their original, respective initial states.

Example 8.10

Discuss an example of a reversible process.

Melting of ice in equilibrium with water at 0 ˚C and 1 atm (Figure 8.8) is a reversible process. At any given moment, a small amount of heat leaves the system, and a small amount of water is frozen to produce ice. During this time, a small amount of heat enters the system through the boundary and melts a small amount of ice into liquid water and both these processes are happening all the time. The key condition is that the temperature of the ice-water mixture is kept constant, despite the heat flow in or out of the system. The phase transition ensures that the temperature is held constant till one of the two phases disappears. Thus, both the system and the surroundings are being restored to their initial states as the forward and reverse processes are taking place. This is a true reversible process because when the surroundings are losing some heat to the bath to melt ice into water, the system is releasing a certain amount of heat to the surroundings by converting a certain amount of water to ice. There has been no net change in either of them. It's a physical equilibrium, and all phase equilibria are reversible processes. That is, there will be no net change either in the surroundings or the system, when the equilibrium has been established. All chemical equilibria, on the same grounds, are also reversible processes.

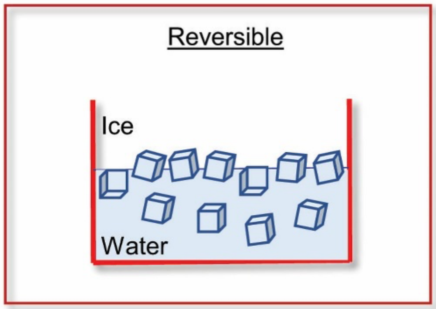

Figure 8.8 An example of a reversible process is the melting of ice at 1 atm, 0 ˚C, in contact with liquid water at the same temperature and pressure. All phase transitions are reversible processes, and all chemical equilibria are reversible processes.

8.4.8 Equilibria

Melting of ice at its melting point, boiling of water at its boiling point, and all such phase transformations are equilibria. We determine that equilibrium is attained when there are no changes in the system as well as the surroundings (Figure 8.7). For this reason, equilibria consist of reversible forward and reversible reverse processes. Both forward and reversible processes are occurring simultaneously, and their rates are exactly equal but opposite in direction. The amount of heat entering the system from the surroundings, for example in the melting of ice above, is exactly equivalent to the amount of heat entering the surroundings from the system due to the freezing of water to ice. If there is any work produced in the surroundings during the forward process, then there will be a corresponding amount of work that is destroyed during the reverse process, as well. Thus, all changes that we can detect either in the surroundings or in the system are equivalent and opposite so that there are no net changes as the equilibrium is established. This is what we define as the equilibrium which consists of reversible processes. A given process is thermodynamically either reversible or irreversible, there is no degree of reversibility. Next, we will define irreversible processes to gain a better insight into these interesting processes.

8.5 Molecular interpretation

Most of the thermodynamic terms and bulk properties have no molecular interpretations. The path a molecule takes from being a reactant to becoming a product is called the mechanism of a reaction. In this sense, we can define path in precise molecular and atomic terms. These details will be discussed under the discipline of chemical kinetics. Initial and final states of the system are also precisely defined in a chemical reaction, in terms of bond distances, bond angles, solvent, and other environmental conditions. These details are discussed under the discipline of quantum chemistry. The initial and final states of a molecule during a spectroscopic transition is discussed under the discipline of spectroscopy and filly described in molecular terms. In a reversible process, the changes are occurring on the infinitesimal scale and the system equilibrates after each of these steps. In an irreversible process, changes are abrupt and either system or the surroundings undergo a net change when the process is reversed. Molecular interpretations help understand the details on a fundamental basis. Thus, thermodynamics has a strong molecular basis that spans most of chemistry, biology, and physics.

8.6 Applications in daily Life

The thermodynamic terms defined here are foundation stones for our discussions of thermodynamics and these are applied in real life as well. Both in the lab and life, these terms are of extreme importance. The importance of paths and processes in daily life is most obvious and they play very important roles in our civilization as well as in many disciplines of science. While reversible processes may seem to be impossible to achieve in reality, we encounter them all the time. For example, all equilibria are reversible processes, and all phase changes are equilibria, which are also reversible. Thus, all other processes are irreversible by the process of elimination. For example, the fall of an apple from the tree, flow of water down the hill, etc., are all irreversible processes. Thus, taking a trip on a plane or a train is an irreversible process, planetary motion is another irreversible process. Our lives are fully bathed in irreversible processes. In later chapters, we will devote more discussion to the irreversible (spontaneous) processes and find a way to predict their feasibility from thermodynamic terms alone. That will, again, demonstrate the power of thermodynamics.

8.7 Key points

1. The definition of the system, boundary, and surroundings is a fundamental requirement for the discussion of the thermodynamics of specific items of interest.
2. A system is simply the region of the universe that is of immediate interest, and it is separated from the surroundings by a boundary. The system and surroundings, together, represent the universe.
3. The system may suffer some changes in its properties such as changes in the pressure or the temperature, and we term this as a change in the state of the system.
4. The initial state of the system is the list of attributes of all the qualities of the system that we are interested in, before the change, and when a change occurs, our system has undergone a change from the initial state to a new state, we call the final state.
5. When a change occurs in the system, it has traveled from an initial state to the final state by traveling via a series of intermediary states and we call this series of states the path.

6. When a system travels from one state to a different state by traveling along a path, we can place specific restrictions on the path, and create specific processes.
7. Equilibria are reversible processes, and a reversible process proceeds in infinitesimal steps while equilibrating at each and every step.
8. After a reversible cycle, neither the system nor the surroundings suffer any permanent change.

8.8 Key terms and units

System, boundary, surroundings, universe, path, change, process, heat, work, and specific heat. The thermodynamic terms we discussed are dimensionless and have no units. Reversible process, reversible cyclic process, irreversible cyclic process, and equilibria.

8.9 Self Reflection

1. Sketch a cartoon showing a system traveling from an initial state to the final state with changes in the surroundings accompanying the change. Carry out this process, under constant pressure conditions or constant volume conditions.
2. Consider the space of your dorm room and identify several cyclic processes, reversible processes, and irreversible processes occurring on a daily or weekly basis.
3. Consider the planet earth as your system with the atmosphere being the surroundings. Identify various thermodynamic quantities entering or leaving the system on a daily or weekly basis.
4. Imagine that you are in a traffic jam in your car and your navigation shows three alternate routes to reach the destination. What thermodynamic parameters would you consider to decide which alternate route to choose from?
5. Imagine that you have sprouted seed in a small pot on your dorm windowsill facing the sun. What thermodynamic quantities enter or leave your system if the pot with the plant is your system?

8.10 Further Reading

1. Physical Chemistry by Castellan, 3rd Edition 1967
2. https://ocw.mit.edu/courses/chemistry/5-60-thermodynamics-kinetics-spring-2008/video-lectures/lecture-2-work-heat-first-law/
3. https://ocw.mit.edu/high-school/physics/exam-prep/kinetic-theory-thermodynamics/laws-of-thermodynamics/8_01t_fall_2004_w13d2_class_32.pdf

8.11 Self Tests

1. System is the space of interest, separated from the rest of the universe by the ______.

a. universe

b. boundary

c. system

d. surroundings

e. none of the above

2. An open system can exchange which of the following with its surroundings?

a. mass

b. energy

c. mass and energy

d. either mass or energy

e. neither mass nor energy

3. An example of a closed system would be:

a. constant volume calorimeter

b. a puddle of water on a hot day

c. a capped glass vial of water on a hot plate
d. both a and c
e. none of the above

4. An example of an isolated system would be:
   a. an icepack in a lunchbox
   b. the earth
   c. constant volume calorimeter
   d. the universe
   e. none of the above
5. An example of a path function would be:
   a. work
   b. energy
   c. entropy
   d. enthalpy
   e. none of the above
6. During an isothermal process the temperature of the system
   a. increases
   b. decreases
   c. stays the same
   d. none of the above
7. During an adiabatic expansion process q = 0, what is the change in the temperature of the system?
   a. increases
   b. decreases
   c. stays the same
   d. none of the above
8. Which of the following is an example of an isobaric process?
   a. Charles' Law
   b. Boyle's Law
   c. Adiabatic process
   d. None of the above
9. Which of the following is an example of an isochoric process?
   a. Charles' Law
   b. Boyle's law
   c. adiabatic process
   d. none of the above
10. Melting of ice in equilibrium with water at 0˚C and 1 atm is
    a. an irreversible process

b. a reversible process
c. adiabatic process
d. equilibrium
e. choices b and d

11. A cyclic process is
a. an irreversible process
b. a reversible process
c. adiabatic process
d. equilibrium
e. none of these

12. A reversible process is
a. one with the same initial and final states
b. multi-step process
c. a process when reversed the surroundings are restored fully
d. a process when reversed the system is restored fully
e. none of these

13. An irreversible process is
a. one with the same initial and final states
b. multi-step process
c. a process when reversed the surroundings are restored fully
d. a process when reversed, either the system or the surroundings are not restored fully
e. none of these

14. A natural process is
a. one with the same initial and final states
b. multi-step process
c. a process when reversed the surroundings are restored fully
d. a process when reversed, either the system or the surroundings are not restored fully
e. none of these

15. The change of state during a process is
a. independent of the path
b. dependent of the path
c. the path itself
d. infinity
e. none of the above

16. For a path function, the change in its value is
a. independent of the path
b. dependent of the path

c. the path itself

d. infinity

e. none of the above

17. For a state function, the change in its value is

a. independent of the path

b. dependent of the path

c. the path itself

d. infinity

e. none of the above

8.12 Self Tests Key

1. b, 2. c, 3. d, 4. d, 5. a, 6. c, 7. b, 8. a, 9. b, 10. e, 11.e, 12. e, 13.d, 14. d, 15. a, 16. b, 17. a

8.13 Problems

1. Examine the system consisting of hydrogen and oxygen reacting in the presence of a Pt catalyst to form water. Analyze if this is a reversible process, after identifying the boundary, path, process, initial and final states. (Hint: Catalysts usually catalyze both forward and reverse reactions at the same time).
2. What is the reason a stone rolling down the hill is not an example of a reversible process? Give full explanation of what is the forward process, reverse process, path, initial and final states.
3. Why is a tub of melting ice in water at 0 K and 1 atm is considered a reversible process but ice melting in a glass of a beverage at room temperature and pressure is not?
4. As the wind blows across, it is a natural process or a spontaneous process. Then, is the air flow from a fan not a spontaneous process or a reversible process?
5. Identify all the irreversible processes that are happening in the space of your dorm room, be as thorough as possible but give at least 3 examples.
6. Analyze a few reversible and irreversible processes occurring daily, on this planet. Explain them in a manner a five-year old can follow.
7. If a spontaneous process is irreversible and happens by itself, what is driving it? Use advanced concepts in future chapters, if needed.
8. Discuss if the earth with its atmosphere is a closed or open or isolated system.
9. When a tank of gas is allowed to escape by opening the valve, the gas escapes spontaneously. Why is the reverse process not observed? That is, gases do not spontaneously enter a cylinder and compress themselves, why?
10. The apple falls from the tree, but it does not fly up and attach itself to the tree. Explain this simple observation by constructing a system, surroundings, path, boundary, initial and final states, and irreversible/reversible processes.

Chapter 9. Heat and Work

After completing this, you will be able to:

- Estimate both heat and work terms for isothermal, isobaric, isochoric, reversible, irreversible, cyclic, natural, and spontaneous processes.
- Determine the maximum amount of pV-work that can be obtained, and the minimum amount of work needed to compress the gas.

Goals

- Synthesize equations and design methods to quantitate heat and work.
- Synthesize mathematical expressions for the work of isothermal and adiabatic transformations.
- Quantify work for cyclic, reversible, and irreversible processes, and compare the work of one-step, two-step, and multi-step expansion and compression.
- Derive equations for the maximum pV-work that can be obtained, and the minimum pV-work needed to restore the system.
- Synthesize equation for the work of cyclic transformations, both reversible and irreversible.

9.1 Why study this?

Several examples of physical processes are examined here, such as the spontaneous expansion of compressed gas, work done during such an expansion, and the maximum work that may be obtained during such an expansion. This expansion work is used in our daily lives to accomplish very simple tasks such as driving to work or school but also extends to very complex tasks such as sending a rocket into outer space. Therefore, a clear understanding of work and its associated properties in specific processes is of fundamental importance, and work could be one of the components of a spontaneous process.

9.2 Heat

We all understand what heat is and appreciate it. Nonetheless, that sort of definition is not adequate for our experimental purposes. We determine the heat produced or heat released in each experiment in a manner that is consistent with our experimental practice.

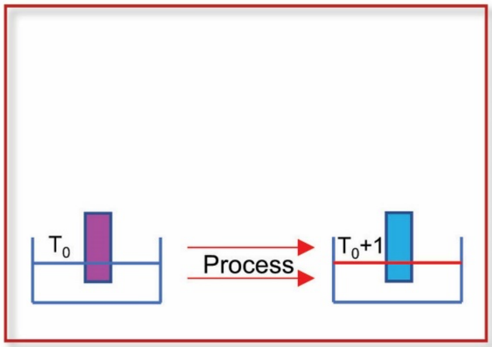

Figure 9.1 Heat is defined as a quantity that is produced at the boundary of a system, during a process, and raises the temperature of a finite mass of water by one kelvin. Heat is an algebraic quantity, and the sign of heat is negative if the temperature of the water is raised. If the heat is absorbed by the system across the boundary during a process by lowering the temperature of a mass of water by 1 K, then the sign of heat is positive.

The heat appears at the boundary of the system during a process, and this is reflected by a change in the temperature of the mass of water in the surroundings. We define heat as an algebraic quantity. It appears during a process at the boundary and is the mass of water needed to observe the temperature change by 1 K. Thus, to emphasize, heat is an algebraic quantity, appears only at the boundary of a system, appears only during a process, and is measured by the mass of water required to raise the temperature by 1 K (Figure 9.1).

To measure heat, we measure the mass of water in the surroundings that has undergone a change in its temperature by 1 K. The sign of heat is automatically determined by the change in the temperature. When the temperature of the water is increased then the sign is negative. The converse is the case when the temperature of the water is decreased during a process. In this case, the sign of heat is positive. This convention becomes clearer in a bit. We give the symbol q for heat and measure q and its sign by simply measuring the mass of water required to change its temperature by 1 K.

9.2.1 The measurement of heat

Let m be the mass of water in grams and S be the specific heat of water, then q is given by the equation below, where the initial temperature is T_1 before the change and the final temperature is T_2 after the change has been completed. The negative sign in the equation ensures that the proper sign convention is followed automatically.

$$q = -(T_2 - T_1)\ m\ S$$

Mass is a positive quantity, specific heat (s) is a positive quantity because heat is to be supplied to raise the temperature of an object, and when $T_2 > T_1$ the sign of q turns out to be negative. Heat leaves the system and appears at the boundary to raise the temperature of water in the surroundings, thereby it increases the temperature from T_1 to T_2. Note that we are using the Zeroth law to measure the temperature and equilibrating our thermometer with the water in the surroundings. Heat appears during a process, and if there is no process, then there is no q, and the initial, as well as the final temperatures, are the same, and q = 0.

Example 9.1

Explain what happens if the temperature of water in the surroundings cools and the sign of q?

When there is a decrease in the temperature of the water in the surroundings, $T_2 < T_1$, during the process, and the sign of q is positive from the above equation. We always measure the mass of water whose temperature change is 1 K, at the end of the process. We simply ask is the heat leaving the system or entering the system. If it is entering the system, then the sign is positive and the system gains that energy, like any other form of energy. If the heat is leaving the system, then the system is losing that energy, and the sign is negative. Thus, it is easier to remember the correct sign if we ask, is the system gaining or losing during the process? The answer guides us to the correct sign.

Example 9.2

Calculate the heat liberated when a coffee cup consisting of 150 g of water cools from 55 ˚C to 25 ˚C.

Heat produced at the boundary of the coffee is = - s m (T_2-T_1) = - 1 cal/(g ˚C) x 150 g x (55-25) ˚C = - 450 cal

9.3 Work

Work is defined as an algebraic quantity that appears at the boundary during a process and changes the height of a mass in the surroundings. Just as heat changes the temperature of water in the surroundings, work changes the height of a mass in the surroundings. When the height of the mass is lowered, work is a positive quantity. When the mass is raised, work is a negative quantity. This sign convention becomes clear when we write the precise mathematical relation, shortly. Thus, we simply measure the height of the mass M in the surroundings to quantify work that appears at the boundary and its sign, during a process.

9.3.1 Measurement of work

Our system consists of a gas sample enclosed in a cylinder with a piston, whose mass is negligible when compared to the mass M above it. The boundary of our system is the surface separating the gas and its physical enclosure, the piston surface, and the inner walls of the cylinder. During the process, let us say that our system expands, undergoes a change from its initial state to a final state, with changes in its attributes as shown in Figure 9.2. The piston can’t move smoothly unless the area of cross section is constant though out the cylinder. During the expansion process, the piston moves up by a certain height (h), work (w) appears at the boundary of the system and raises the center of mass M by a certain height h, performing work. Mass is raised, and hence the sign of q is negative, from the above convention.

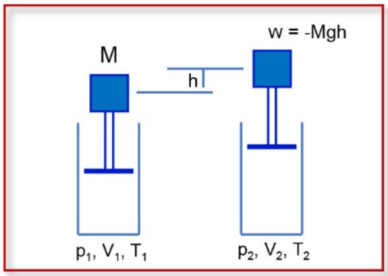

Figure 9.2 Consider a sample of gas in a cylinder enclosed with a piston and a piece of mass (M) on the top of the piston. When the gas expands from the initial state p_1 v_1 and T_1 to p_2 V_2 and T_2, the work that appears at the boundary during the expansion process (w) is – M g h where, g is the acceleration due to gravity, and h is the vertical height through which the center of the mass M is moved. We assume that the mass of the piston is negligible when compared to that of M. Let A be the uniform area of cross section of the cylinder.

Consider the opposite scenario, where the final state is converted to the initial state and the mass is lowered by a height h, in the reverse process. In this case, work appears at the boundary and the work has a positive sign because mass M is lowered. In both cases, work appeared at the boundary during a process. No process, no work, and work always manifests as a change in the height of a mass in the surroundings. Work is an algebraic quantity, and we can perform the sum or subtraction operations. This is our definition of work, and we use gases and masses to measure the work and its sign.

Example 9.3

Discuss other forms of work and relate to pV work.

Even though we define work in terms of the change in the height of a mass in the surroundings, we can readily convert this into other types of work. For example, an electrical motor might lift a mass in the surroundings, and we can determine the work done by the motor. Similarly, there could be other forms of work that can be converted into this type of measurement. For example, our gas expands and performs the pressure-the volume work lifting mass M, and we can determine the work that appears at the boundary during the expansion process or a compression process, the pressure-volume work. So, for convenience, we will convert this mechanical measurement of work in terms of pressure and volume. Thus, we convert the change in the height of the mass in the surroundings into changes in the properties such as the pressure acting on the gas and the change in gas volume, during a process.

9.3.2 Measurement of the pressure-the volume work

We begin with the definition of work from physics as the force times distance of displacement of the mass, and then compute the fo4ce and the distance. The following simple steps can quickly connect the work with the area of the cross section for a cylinder with mass, M, height, h, and the volume change. The negative sign is consistent with our convention and will become clear soon.

$$\mathrm{w} = \text{force x distance} = -\,\mathrm{M\,g\,h}$$

$$\mathrm{w} = -\,(\mathrm{M\,g\,/A})\,\mathrm{h\,A}$$

In the above expression, we replace the force with M g, the gravitational force acting on the mass M, on planet earth. The negative sign indicates the inverse relation between the work and the height. When the height is positive, the mass is raised, the work appears at the boundary, and has a negative sign.

Next, we divide the force with the areas of cross section of the piston (A) and multiply with A, so that there is no net change on the right side of the equation. Then, we recognize that height times A is the change in the volume $(V_{final} - V_{initial})$, as the gas expands or compresses. Next, we recognize that force per area is the pressure applied by the piston on the gas sample or the external pressure against which the gas is expanding (p_{ext}). Now, we indicate the volume change as ΔV and write the expression for w, as following.

$$\mathrm{w} = -\,p_{ext}\,(V_{final} - V_{initial}) = -\,p_{ext}\,\Delta V$$

We simply replaced the force and the height with parameters related to the system, the external pressure exerted by the piston on the gas, and the change in the volume during the process. The units of work then, correspond to those of the pV or the pressure-the volume work. Note that it is not the gas the pressure that we are using in the above expression but the pressure due to the force of gravity applied by the Mass M over the area of cross section of the cylinder (p_{ext}).

Example 9.4

Calculate the work done when a gas expands from an initial volume of 5 liters to a final volume of 15 liters against an external pressure of 1 atm, at constant temperature and mass.

Work = - external the pressure x change in the volume = - p_{ext} (V_{final} – $V_{initial}$) = - 1 atm x 10 L = - 10 atm L

We look in the surroundings and ask, what is the external pressure against which the gas is expanding and how much is the change in the volume of the gas to compute w? If the volume change is positive, the mass is raised in the surroundings, work appears in the surroundings, and hence, the sign of work is negative.

On the other hand, when the volume change is negative, the final volume is less than the initial volume, $\Delta V<0$, and the gas has been compressed. A certain amount of work has appeared at the boundary and masses are lowered in the surroundings and w has a positive sign. The sign of work is automatically assigned by the changes in the properties of the system, and we need not ask if work is destroyed or created in the surroundings. We ask, are the masses raised or lowered in the surroundings during the process and then determine the sign with the above convention.

We simply ask whether the work is leaving the system or entering the system, just as any other form of energy. If the system gains work, it is positive, and if the work leaves the system, then it is negative. This is clearer than asking if the work is done by the system or work is done on the system. The signs are arbitrary and until 1967, the sign of work is opposite to what it is now. But this change has not affected thermodynamics or its validity. For example, the textbook by Castellan written in the 1960s has the opposite sign for w as compared to the modern convention given here, but it is the same thermodynamics that is applied today as it was then.

9.3.3 Work for infinitesimal changes in the volume

The above expression provides work that appears during a finite change in the volume. We can now write an expression for work that appears at the boundary during an infinitesimal change in the volume, by re-writing the expression in terms of infinitesimal changes. The infinitesimal change in work (dw) is given by the infinitesimal change in the volume (dV) when the process is progressing by an infinitesimal increment, as given below.

$$\mathrm{dw} = -p_{ext}\, dV$$

The infinitesimal change in work is then given as the product of the external pressure and the infinitesimal volume change and the negative sign is left as is. The external pressure is constant throughout our expansion, and hence, there is no differential sign applied to it. This kind of process is used often in our discussions and needs to be recognized with care.

In summary, work is an algebraic quantity that manifests at the boundary of the system, during a process and is quantified by monitoring the height of a mass is raised or lowered in the surroundings. Work appears only during a change, no change no work. Work is negative when raising masses in the surroundings and it is positive when the masses are lowered. There are other forms of work, such as electrochemical, photochemical, biochemical, etc., but we are not concerned about these here.

9.4 Isothermal Compression Work

We will take specific processes to dissect the work produced or destroyed during a process. In compression, the opposing pressure (p_{opp}) must be greater than the initial (p_1) and final the pressure of the gas (p_2), in our system. We will examine different versions of the compression work separately.

$$p_{opp} > p_2 > p_1$$

9.4.1 Single-step compression work

Since the opposing pressure due to the piston on the gas in the cylinder is greater than the gas pressure throughout the compression process, the gas will undergo compression, spontaneously. The compression of the gas stops when the gas pressure and the opposing pressure are exactly equal, thus, the final pressure of the gas can be exactly p_{opp} if we like, or greater. Thus, the volume will change from an initial value (V_2) to a final value (V_1).

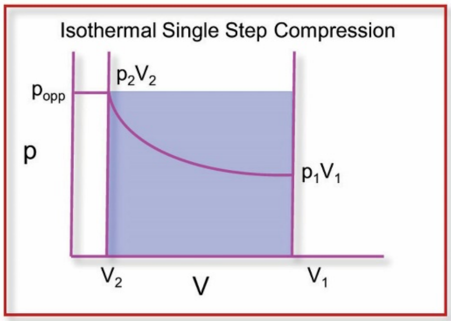

Figure 9.3 The work of compression by opposing the pressure (p_{opp}) with the volume changing from V_1 to V_2, while the gas pressure changes from p_1 to p_2.

The work done during the isothermal compression of a gas is shown graphically in Figure 9.3. This is a plot of the pressure vs the volume, and the initial state is given by p_2 and V_2. When the opposing pressure (p_{opp}) is greater than gas the pressure p_2, the compression begins and continues till the gas the pressure p_1 equals the opposing pressure. Thus, if we want to compress the gas all the way to volume V_1, in a single step, then we need to make sure that the opposing pressure is at least equal to the final pressure p_1. When the opposing pressure is equal to the final pressure, then the compression ends, and the system reaches the pressure p_1 and volume V_1. The opposing pressure can be greater than the final pressure, but then the compression needs to be stopped by some other means, such as a plug that stops the piston from moving any further.

By using the expression for the pressure-volume work, arrived above, we calculate W, as following.

$$W = - p_{opp} (V_1 - V_2)$$

$$p_{opp} \geq p_1$$

Since the final volume is less than the initial volume (compression), the work of compression is positive, and the masses are lowered in the surroundings. The entire compression is completed in one step, under constant temperature conditions. The blue area enclosed by the rectangle with limits p_{opp}, V_1, and V_2 is the magnitude of the compression work, $p_1 = p_{opp}$. When p_{opp} is greater than p_1, then the magnitude of the work will be larger than the blue rectangle shown. The compression work can also be carried out by a two-step process, as discussed below.

9.4.2 Two-step compression

Imagine that we stop the compression at an intermediate step of p'_{opp} with an intermediary the volume of V' and then complete it to achieve the final state p_2, V_2 (Figure 9.4). We start with the volume V_1 and compress it with an opposing the pressure of p'_{opp} to the intermediary the volume V' and the gas the pressure at this intermediary state is p'_{opp} because the compression stops when the gas pressure is equal to the pressure of compression. The work destroyed in this first step is given by the purple rectangle. We, then compress the gas further, with p_{opp}, in the second step from V' to the final volume V_2. The compression stops naturally, when the pressure of compression equals the gas the pressure, p_2. Work for the second step is given by the blue rectangle, by analogy with the previous examples and the mathematical equations outlined below.

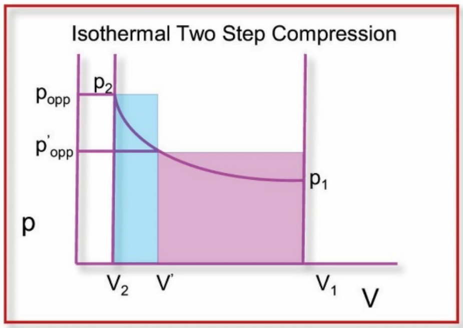

Figure 9.4 Work in a two-step compression with an intermediary state of volume V'. The total work is the sum of the areas of the two rectangles, purple, and blue. This is less than the area of the single-step compression, blue rectangle, shown in Figure 9.3.

The compression work will be the sum of the work done in the first step, w_1 plus the work done during the second step w_2, and the total work w for the two-step compression is the sum, as given below.

$$w_1 = -\, p'_{opp}\,(V' - V_2)$$

$$w_2 = -\, p_{opp}\,(V_1 - V')$$

$$w = w_1 + w_2 = -\, p'_{opp}\,(V' - V_2)\; -p_{opp}\,(V_1 - V')$$

The work terms for the first step and the second step, as expected, contain the respective opposing pressures. The total work of compression for the two-step process is the sum of the two work terms and this is equal to the sum of the areas of the two rectangles (blue and purple) in Figure 9.4. We recognize that the total area of these two rectangles is still less than the blue rectangle in Figure 9.3 and this is because the first step of compression required much less pressure than the one step compression. Thus, much less work appears at the boundary in compressing the gas from the same initial state to the final state in a two-step process. The sign of work is positive because each of the work terms is positive. This becomes immediately clear because the final volumes are less in each step and the volume is decreasing, making both ΔV terms negative and this cancels out with the negative signs in front of each work term. Thus, the total work is positive as well. Thus, masses need to be lowered to compress a gas, and this is our common experience, gases don't compress themselves spontaneously.

Comparing the one step and two step compression processes, we immediately recognize that work is not a state function, but it depended on the path we have taken to achieve the final state. Thus, work is a path function. We can also show this algebraically by comparing the expressions for work corresponding to the two paths. The value of p'_{opp} is much less than p_{opp} and hence, the sum of the two terms for the two-step compression is less than the single term in the work for one step compression. If we can compress the gas by two or more steps, we should also be able to compress the gas by infinitesimal steps or by a new and interesting process, described below.

9.4.3 Infinite step compression

The isothermal compression can be carried out by adjusting the opposing pressure (p + dp) such that it is infinitesimally greater than the gas the pressure p, and this allows the gas to be compressed by an infinitesimal decrease in the volume V – dV and increase in gas the pressure to p + dp (Figure 9.5).

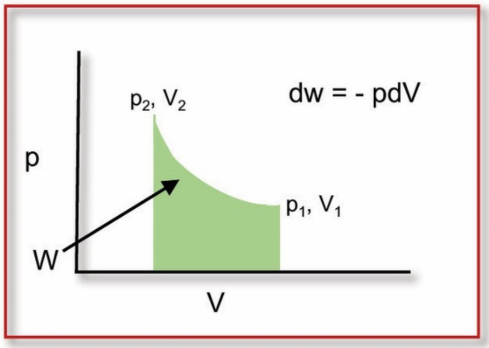

Figure 9.5 The work of reversible compression for an ideal gas. The green enclosed area represents the magnitude of the work of compression. This is the least amount of compression work of all the three cases discussed.

The work done on the system at the end of each infinitesimal step is then given by the following equation.

$$dw = -\, p'_{opp}\,(dV) = -\,(\mathrm{p} + \mathrm{dp})(dV)$$

$$dw = -\,p\,dV - dp\,dV$$

$$dw = -\,p\,dV$$

Note that the p'$_{opp}$ is replaced by p + dp so that the compression takes place by an infinitesimal amount. In the subsequent step, we expand the parenthesis and recognize that we have the dp dV term. It is immediately clear that this product must be close to zero because dp is infinitesimal and dV is infinitesimal and hence, their product must be much less than either of these quantities, close to zero or it can be neglected for all practical purposes. Thus, the infinitesimal work that appeared at the boundary is now expressed in terms of gas the pressure and change in volume. This happened only because the p$_{opp}$ is only infinitesimally larger than p, and the product of two infinitesimal quantities can be neglected.

After the first step of compression by an infinitesimal amount, the system is equilibrated and compression is continued by increasing the opposing pressure by another infinitesimal amount greater than the gas pressure, after the first infinitesimal step. Thus, we continue to increase the opposing pressure by infinitesimal amounts, each time, continue to compress by an infinitesimal decrease in the volume at each step, and hence, the work is simply an integral of pdV. Keep in mind that the opposing pressure must be greater than the pressure of the gas, otherwise the gas will not be compressed by the opposing pressure.

$$\mathrm{W} = -\int_2^1 p_{opp}\,dV$$

We can integrate this expression with the limits of initial (1) and final (2) states, where the opposing pressure is replaced by the gas the pressure at each of the intermediary states, and hence, a variable itself.

$$\mathrm{W} = -\int_2^1 (\mathrm{p}+\mathrm{dp})\ \mathrm{dV}$$

$$\mathrm{W} = -\int_1^2 \mathrm{p\ dV} - \int_1^2 \mathrm{dp\ dV} = -\int_1^2 \mathrm{p\ dV} - 0$$

However, the integration of the above function is possible only after we express the pressure in terms of volume. For an ideal gas, we can do so readily. If the gas is not ideal, then we need to write the pressure as a function of the volume using a suitable equation of state, before integration, the ideal gas law.

$$\mathrm{W} = -\int_2^1 (\mathrm{nRT/V})\ \mathrm{dV}$$

$$\mathrm{W} = -\,\mathrm{n\,R\,T}\ln(\mathrm{V_1/V_2})$$

The integration gives the final expression above, and the work of reversible compression is shown in Figure 9.5. The green enclosed area represents the work of compression, and as we compare the areas of work of the above three methods, the smallest in magnitude is the infinitesimal step compression.

Comparing Figures 9.3 through 9.5, we recognize that the least amount of work is needed to compress an ideal gas when the compression is carried out in infinitesimal steps. Again, the single step compression work is the largest, while that of the infinitesimal step compression is the least. Thus, work is a path function, and its magnitude depends upon the path chosen to connect the initial and final states.

$$W_{infinite\ step} \ll W_{two\ step} \ll W_{single\ step}$$

In summary, we say that the work of compression is always positive. That's because we are compressing the gas by lowering the masses in the surroundings. The work of compression is the least when we carry out the compression by infinitesimal steps.

9.5 Isothermal Expansion Work

Similar to the compression process discussed above, we can carry out the expansion process also by a variety of methods. We will construct one step, two step, and infinitesimal step expansion and examine the work produced or destroyed during these processes. This is of practical importance, and we often encounter this process in our daily lives.

9.5.1 One-step expansion

As in the case of compression work, the initial state is p_1, v_1, and the final state is p_2, V_2 but notice that $V_2 > V_1$ because it is expansion, but $p_1 > p_2$, at constant the temperature and mass. As before, imagine that the gas sample is enclosed in a cylinder fitted with a mass-less and friction-less piston, and a mass M is placed on the piston. As the gas is allowed to expand, mass is pushed up because p_{opp} is less than the gas the pressure, or else expansion can't occur. At the end of the expansion, the p_{opp} is equal to the final pressure p_2, and the expansion will stop due to the equalization of the pressures at the final state. If the gas pressure is still greater than the opposing pressure, then we need to stop the piston from moving any further up. The work of single step expansion is then, given as below.

$$w = -\,p_{opp}\,(V_2 - V_1)$$

$$p_2 \geq p_{opp}$$

The final volume is greater than the initial volume and hence, w is <0 or that work has appeared at the boundary and the masses are higher in the surroundings. This is consistent with the expansion work and raising of the mass M in the surroundings.

We represent this process as the pV plot, shown in Figure 9.6. This is a plot of the pressure vs the volume from the initial state to the final state, one-step, isothermal expansion of any gas. The opposing pressure is less than or equal to the gas the pressure of the final state. When it is equal, the expansion will stop but when the opposing pressure is less than the final pressure, efforts are to be made to stop the piston from moving further up.

$$W = -\,p_{opp}\,(V_2 - V_1)$$

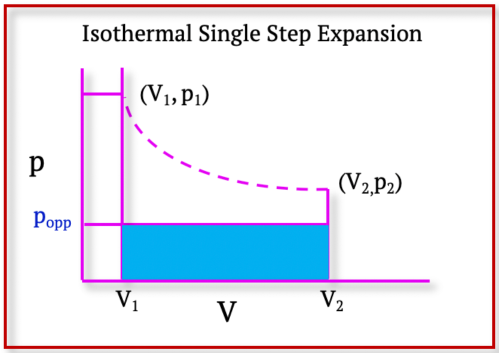

Figure 9.6 **I**sothermal, single step expansion of a gas against an opposing pressure which is equal to or less than the final pressure. The final volume is greater than the initial volume and hence, the magnitude of the work (blue rectangle) is negative or that some work has appeared at the boundary and the masses are higher in the surroundings.

The magnitude of the work of single step expansion is the product of the opposing pressure and the change in the volume, and that is exactly equal to the blue rectangle shown in Figure 9.6. Compare this with the work for the single-step isothermal compression shown in Figure 9.3, which is much larger and the reason for this is clear, the differences in the magnitudes of the opposing pressures. Thus, it requires much more work to compress the gas than to allow it to expand, and we will comment on this observation much later.

9.5.2 Isothermal, two-step expansion

Similar to two-step compression, we can design a two-step expansion and compare the corresponding work terms (Figure 9.7). The work of two-step expansion is the sum of the work done in the first step and the work done in the second step, or break it down into two, separate single-step expansions, which we already discussed. The initial state is still p_1, V_1, and the final state p_2, V_2. The system expands in the first step to an intermediary the volume V_i against an opposing the pressure p'_{opp}, until the gas the pressure equals the opposing the pressure, and the opposing the pressure needs to be greater than the final pressure, p_2 or else expansion will continue to the final state in the first step itself.

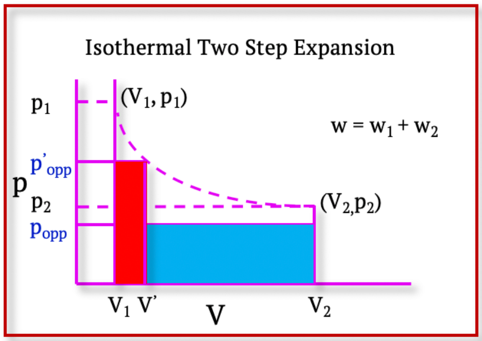

Figure 9.7 Two-step expansion of a gas, first to an intermediary state (red rectangle on the left) followed by expansion to the final state (blue rectangle at the bottom). If the p_{opp} is less than the final pressure, p_2, then the piston needs to be stopped from moving any further. The crankshaft of an automobile engine restricts the motion of the pistons in the cylinders, in this manner.

The work of expansion of the first step is given by our standard expression, given below.

$$w_1 = - p'_{opp} \, (V_i - V_1)$$

The work of expansion is negative, the masses are raised in the surroundings and the pressure-the volume plot is shown in Figure 9.7. The expansion work for the first step is shown by the red rectangle and note that the final pressure is less than the opposing pressure.

After the first step, the opposing pressure is allowed to decrease to p_2, and the expansion is allowed to complete in the second step from V_i to reach the final volume V_2. The work of expansion in the second step and the work done in the two-step expansion are given by the following equations.

$$w_2 = - p_{opp} \, (V_2 - V_i)$$

$$W = w_1 + w_2 = - p'_{opp} \, (V_i - V_1) - p_{opp} \, (V_2 - V_i)$$

The sign of work in the second step is also negative, because the final volume is greater than the intermediary volume, and the masses are raised in the surroundings. The work of two step expansion which is the sum of the work from the first and second steps is also negative because each of these two terms is negative. Thus, the net effect is that the masses are raised in the surroundings. Yet, there is another interesting feature of the two-step expansion.

$$W_{two\ step} \ll W_{single\ step}$$

Note that the sum of the areas of the purple and the blue rectangle represents the total work of compression in a two-step compression (Figure 9.4). Obviously, the sum of the two areas is larger than the area of the two-step expansion, blue rectangle in Figure 9.7. However, the sign of work is negative, and this is also clear from the equations of work that we have deduced above. Thus, more work is produced in the surroundings in a two-step expansion, than in a single step expansion. Analysis along these lines of work of expansion by multi-step process may even be larger and this is what we will examine next.

9.5.3 Isothermal, infinite step expansion

Here, we examine the multi-step expansion where each step is an infinitesimally small step, we have an infinite number of steps between the initial and final states, an infinitesimal amount of work is done in each step by lowering the opposing pressure to be less than gas the pressure by dp. Thus, mathematically, this process implies that the work done from the initial state to the final state is the integral of dw with limits of initial state to the final state, where dw is the infinitesimal amount of work performed by the system in each step of expansion. This scenario is described by Figure 9.8 and by the following equations.

$$\mathrm{W} = -\int_1^2 dw = -\int_1^2 (\mathrm{p} - \mathrm{dp})\, \mathrm{dV}$$

We pay attention to the opposing pressure which is p - dp so that at every step of the expansion, the opposing pressure is less than the gas pressure by an infinitesimal amount. This way, the gas expands by only an infinitesimal increase in the volume, equilibrated, and then the opposing pressure is reduced by an infinitesimal amount to continue the next step of expansion. The opposing pressure is continually changing as the gas is continuously expanding, justifying the integration of the work expression. The above integral is further transformed to write the p dV and dp dV terms as follows.

$$\mathrm{W} = -\int_1^2 (\mathrm{p\,dV} - \mathrm{dp\,dV})$$

$$W = -\int_1^2 \mathrm{p\,dV} = -\int_1^2 \frac{\mathrm{nRT}}{\mathrm{V}}\, \mathrm{dV}$$

We expand the parenthesis in the integral and recognize that dp dV is negligible, as this is the product of two infinitesimal increments. We write the above integral in a more simplified manner, but we still can't integrate this expression because p is a variable, and it needs to be expressed in terms of the volume. To do this, we assume that our gas is ideal and use the ideal gas law and write p as equal to nRT/V, as we did earlier, and then proceed to integrate between the initial and final states.

$$\mathrm{W} = -\mathrm{n\,R\,T}\int_1^2 \frac{1}{V}\, dV = -n\,R\,T\,ln(V_2/V_1)$$

We recognize that this is the work of expansion when we use ideal gas in our cylinder, but for all the other gases, we need to express the pressure in terms of the volume with an appropriate equation of state, such as the van der Waals equation or another as needed. We also recognize that the sign of work is negative, and the masses are raised in the surroundings, as the gas expands, pushing the piston upward. This scenario is illustrated in Figure 9.8, further.

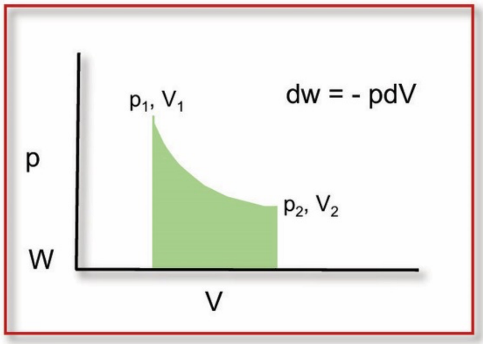

Figure 9.8 The work of expansion of an ideal gas from the initial state to the final state by infinitesimal steps.

The pV plot for the infinitesimal step expansion from the initial state to the final state is shown in Figure 9.8. The opposing pressure is smoothly and continuously decreasing from value p_1-dp to p_2-dp and at each step, the opposing pressure is infinitesimally less than that of the expanding gas. For this reason, we can integrate the expression for work, and to do that we expressed the pressure in terms of the volume using the ideal gas law. Thus, we can consider that there are infinite steps in the expansion, each step contributing the area of a rectangle that is of infinitesimal area. The corresponding limits of the integral are the initial and final states. Therefore, we get the final expression which corresponds to the area under the pV curve.

$$\mathrm{W}_{expansion} = -\mathrm{n\,R\,T}\ln(V_2/V_1)$$

Because this is expansion, $V_2 > V_1$ and hence, the value of the logarithm in the above equation is positive and the sign of work is negative, or the system loses work. This deduction is consistent with the one step and two step expansions we discussed before, and by comparing the corresponding figures, we recognize that the area under the curve of the infinitesimal expansion is the largest and write the following relation because W is negative for each of these terms.

$$W_{infinite\ step} \ll W_{two\ step} \ll W_{single\ step}$$

Summarizing, the isothermal expansion work is always negative because the gas is expanding, so the masses are being raised in the surroundings. The maximum amount of work is produced in the surroundings when the expansion is carried out by infinitesimal steps, or the masses are raised the furthest. We also conclude that the work of expansion depends on the path used, and this is similar to the conclusion we arrived at when examining the work of compression. Thus, work is a path function but not a state function. For certain paths, work can be a state function, and we will see an example in the next section.

Example 9.5

Calculate the work done when a gas expands reversibly from an initial volume of 5 liters to a final volume of 15 liters, at a constant temperature of 300 K and mass of 1 mole.

Work done = - external the pressure x change in the volume = - nRT ln (V_{final} / $V_{initial}$) = - 1 atm x 10 L = - 15 atm L

9.6 Work of cyclic transformations

The cyclic transformations consist of a forward process and a reverse process or that the system travels through several steps only to return to the initial state. This is like a fish in a bowl, swimming and swimming all day but not going anywhere. Thus, the initial and final states of the system are identical in a cyclic transformation, but the system must travel through a path and undergo changes that ultimately restore the system. Note that we emphasize the system and not the surroundings because there could be permanent changes in the surroundings in a cyclic transformation but there can’t be any changes in the system.

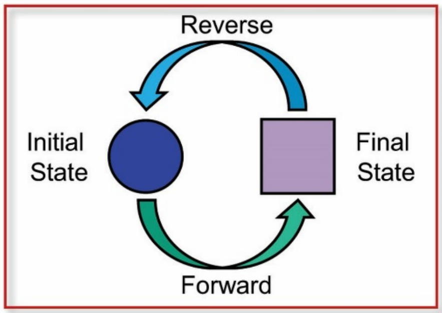

Figure 9.9. Cyclic transformation consisting of a forward process (bottom green arrow) during which the system travels to the final state and a reverse process (top blue arrow) during which the system returns to the initial state. Note that the forward and reverse steps need not be reversible, or the same, in a cyclic transformation. Also, note that we do not consider the status of the surroundings in a cyclic transformation, we only evaluate the system passing through the cycle.

The initial and final states are connected by a forward process and there is a reverse process that connects the final state with the initial state (Figure 9.9). The forward process makes certain changes in the system, and the reverse process restores the system back to its original state. However, we have no information about the surroundings, and we do not particularly need that unless we are interested.

Example 9.6

Explain what happens to the system as it runs through many irreversible, cyclic transformations?

We can take the system through infinite cycles, in principle, and return it back to its initial state with no changes in it. This is desirable and very useful in producing work in the surroundings or converting something to another, again and again, without any loss in the properties of the system. For example, the automobile engine runs through millions of such cycles during its life span, so does the steam engine or the turbines of a jet. Cyclic transformations are of crucial importance for all such critical applications in our daily life. Thus, thermodynamics takes a center stage in practical applications.

In addition, the cyclic transformation also plays a very important role in our investigations of thermodynamics, and it provides a method to determine if a property of the system is a state function or a path function. We can construct cyclic transformations, for example, and test if work is a state function or a path function. Since work is an algebraic function, we wrote earlier that the work for a cyclic transformation is the sum of the work for the forward process and the work for the reverse process, as shown below.

$$W_{cycle} = W_{forward} + W_{reverse}$$

We will calculate W for three specific cyclic transformations, outlined below.

9.6.1 Cyclic, single-step expansion followed by single-step compression

Consider a cyclic process for a sample of gas enclosed in a cylinder with a piston, where the forward process is a one-step isothermal expansion from the initial the volume V_1 to final the volume V_2, and the reverse process is the one-step isothermal compression which restores the system back to its original state (Figure 9.10). We have the initial state p_1V_1 and the final state p_2V_2, and during the forward process the gas is expanding and hence, V_2 is greater than V_1.

Applying Boyle's law, we conclude that p_2 must be less than p_1, and hence, we have the forward process shown by the green rectangle. This requires that the opposing pressure for the expansion ($p_{expansion}$) be at least as low as p_2 or else expansion will stop before reaching the final state. Now, we look at the isothermal compression where the opposing pressure ($p_{compression}$) should be at least as large as p_1, or else the compression will stop before reaching the initial state.

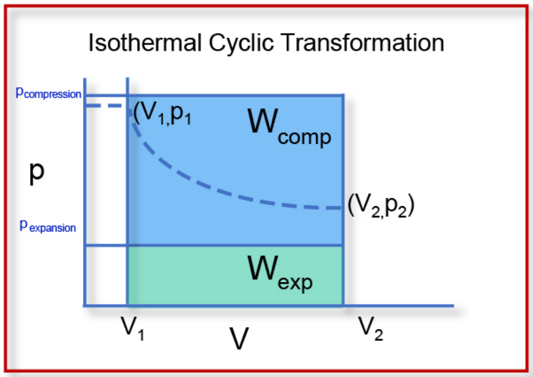

Figure 9.10 The work of isothermal one-step expansion and one-step compression cycle is greater than zero. Note that the bottom part of the work of compression rectangle completely overlaps with that of work of expansion rectangle (not shown).

The opposing pressure in the expansion ($p_{expansion}$) has to be such that it is less than the internal pressure of the system, and during the compression, the opposing pressure ($p_{compression}$) has to be greater than the gas the sure. As we move forward, we are expanding the gas during which the masses are raised in the surroundings, and as we travel along the reverse process, the gas is being compressed back to the initial state, and masses are lowered in the surroundings. Thus, W_{cycle} for this cyclic process of isothermal/expansion/compression is given by the sum of the work for the expansion ($W_{expansion}$) and the work for compression ($W_{compression}$).

$$W_{cycle} = W_{expansion} + W_{compression}$$

Previously, we have deduced the work of expansion for an isothermal single-step process and single-step isothermal compression. Thus, we write the expression for cyclic work for this cycle as given below.

$$\mathrm{W}_{cycle} \ = -\, p_{expansion}\,(V_2 - V_1) - p_{compression}\,(V_1 - V_2)$$

Since the volume changes are the same, we can re-write the second term so that we can take the volume change out.

$$\mathrm{W}_{cycle} \ = -p_{expansion}\,(V_2 - V_1) + p_{compression}\,(V_2 - V_1)$$

$$\mathrm{W}_{cycle} \ = (V_2 - V_1)(p_{compression} - p_{expansion})$$

We recognize that the volume change is positive and that the pressure required to compress the gas in one step isothermal expansion has been far greater than the opposing pressure in the corresponding one-step expansion. Thus, both terms are positive, and their product is positive, and therefore, W_{cycle} is >0. Masses are lowered in the surroundings, in these cyclic transformations. These steps and the cyclic work for this process are illustrated in terms of the pV diagram (Figure 9.10).

The sum of the areas of the blue rectangle and the green rectangle should be equal to the work of compression for the cycle. Thus, we can see that the work of compression is much larger than the work of expansion, and the W_{cycle} must be larger than zero.

$$W_{cycle} > 0$$

Therefore, we can conclude from the cyclic transformation that masses are lowered in the surroundings when the system goes through each of these isothermal cycles. Since W_{cycle} is not equal to zero, it is not a state function.

9.6.2 Cyclic, isothermal, two-step compression followed by two-step expansion

This process is similar to the above case, except that there are two separate steps in the forward and reverse processes, instead of single steps (Figure 9.11). Thus, the forward process takes the system from the initial state to the final state via an intermediary expansion state, before reaching the final state. Analogously, the reverse process employs two separate steps of compression, so that it stops at an intermediary state before reaching the initial state. Thus, we track all the volume changes and the required opposing pressures for each of these four steps, and calculate w for each of these steps, and add them together to obtain w for this cyclic process.

$$W_{cycle} = w_1 + \, w_2 + \, w_3 + \, w_4$$

We define the opposing pressures for each of the steps such that the appropriate intermediary steps exist. We pick $p'_{expansion}$, $p_{expanson}$, $p'_{compression}$, $p_{compression}$ as the corresponding opposing the pressures, V' the intermediary the volume during the forward process, and V" as the intermediary the volume during the reverse process. Then, we calculate the corresponding work terms and then finally sum them.

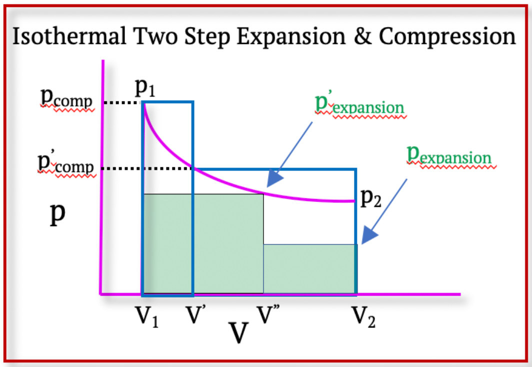

Figure 9.11 The work of two-step expansion followed by two-step compression. The sum of the areas of the green rectangles is less than the sum of the areas of the purple rectangles.

$$W_1 = -\,p'_{expansion}\ (V' - V_1)$$

$$W_2 = -\,p_{expansion}\ (V_2 - V')$$

$$W_3 = -\,p'_{compression}\ (V'' - V_1)$$

$$W_4 = -\,p_{compression}\ (V_2 - V'')$$

$$W_{cycle} = -\,p'_{expansion}\ (V' - V_1) - p_{expansion}\ (V_2 - V') - p'_{compression}\ (V'' - V_2) - p_{compression}\ (V_1 - V'')$$

These steps are illustrated in Figure 9.11 where the green rectangles corresponding to the expansion and the blue, purple rectangles corresponding to the reverse process. It is clear from comparing the areas of the rectangles that the work of the forward processes outweighs the reverse processes. Thus, W_{cyle} is again >0 and for each cycle, the masses are lowered in the surroundings.

Thus, in both the above cases, there is a net amount of work that appears at the boundary, and masses are lowered during each cycle. Even though the system is restored after each cycle, there is a net change in the surroundings during each cycle. In each of the above cases, the W cycle is not the same, and hence, work for these processes is not a state function. In addition, we also recognize that both the above cyclic processes are irreversible because there have been net changes in the surroundings during each cycle.

Example 9.7

Calculate W_{cycle} when an ideal gas undergoes the above reversible transformation to the final state and then back to the initial state by irreversible, one step compression where $p_{opp} = p_{final}$.

$W_{cycle} = w_{forward} + w_{reverse} = -\ nRT \ln (V_{final} / V_{initial}) + p_{final}(V_{final} - V_{initial})$ atm L

9.6.3 Reversible cycles

Here, we examine the isothermal reversible expansion and isothermal reversible compression which form a reversible cyclic transformation (Figure 9.12). The forward process involves infinitesimal steps of expansion from the initial to the final state, under reversible conditions, and the reverse process involves infinitesimal steps of compression from the final state, back to the initial state. As the transformations proceed, only reversible changes occur and after the forward process is reversed, the system, as well as the surroundings, are fully restored to their original respective status.

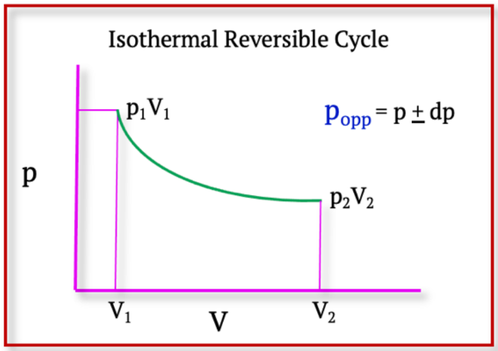

Figure 9.12 Isothermal reversible expansion, followed by isothermal reversible compression of an ideal gas. The work done during the forward process (under the green curve) is exactly equal but opposite to that in the reverse process, thus, w for one complete cycle is zero. Then, w for the forward or the reverse process of this cycle is a state function.

We allow the system to expand by a small increase in the volume, dV in each of the steps until it travels from the initial state to the final state (Figure 9.12). In the reverse process, we allow the system to be compressed by -dV all the way from the final state back to the initial state. Thus, the work done during this cycle is the sum of the work for the expansion process and the work for the compression process, each of which is reversible. Thus, we have infinitesimal changes and so work is obtained by integrating -pdV over the initial and final states, for each of the two processes. Thus, we write the following expression, based on our previous discussions.

$$W_{cycle} = -\int_1^2 p\,dV - \int_2^1 p\,dV$$

The initial state 1 and the final state 2 are the limits, and we recognize the forward, and the reverse steps have opposite limits. Note that the pressure term in the expansion is the same as the pressure term in the compression term, and both are equal to the gas pressure at each step of either process. We have already deduced these details earlier and integrated these expressions for an ideal gas, as follows.

$$W_{cycle} = -\,\mathrm{n\,R\,T}\ln(V_2/V_1) - \mathrm{n\,R\,T}\ln(V_1/V_2) = 0$$

The two logarithmic terms cancel away, and the cyclic work of this transformation is zero. The above mathematical equation is illustrated as the pV diagram, at constant the temperature and mass (Boyle's law), in Figure 9.12. The initial and final states for the forward process are (p_1, v_1) and (p_2, V_2), and the smooth line connecting the two states (Boyle's law curve) is the path representing the intermediary states where each step is reversible. Therefore, the entire cycle is also reversible.

The area under the curve between the initial and final state is the value of the integral and it is the magnitude of the work for the process. The forward process is expansion, and hence, it has a negative sign, and the reverse process is compression with a positive sign. However, the area under the curve for the forward process is the same as the area under the curve for the reverse process, and hence, the work done for the cycle is exactly equals to zero. Thus, W_{cycle} is a state function. Work is normally a path function and depends on the path connecting the initial and final states, but here the path is defined to be a reversible process, and due to the reversibility requirements, work became a state function. Not all cycles are reversible, and hence, work is normally a path function, and only for reversible processes, it is a state function. If we simply fix the path, work does not become a state function, as we proved in two separate cases, above.

$$\mathrm{W_{cycle}} = 0,\ \text{reversible cycle}$$

In summary, we have shown the work done in different cyclic transformations, and unless the cycle is reversible, work is not a state function. For all reversible cycles, work is a state function and for all others, work is a path function.

Example 9.8

Calculate W_{cycle} when an ideal gas undergoes the transformation in the previously example, reversibly to the final state and then back to the initial state by reversible compression.

$W_{cycle} = w_{forward} + w_{reverse} = -\ nRT\ ln\ (V_{final} / V_{initial}) + nRT\ ln\ (V_{final} / V_{initial}) = 0$ atm L

9.7 Molecular interpretation

However, the molecular descriptions of heat and work are in order. Heat is the manifestation of the random motion of the molecules while work is the directed motion of the molecules. Thus, these two types of motion differ in terms of the direction the molecular travels. For example, work involves the coordinated motion where most molecules, at least, are moving in the same direction or that they have a major component of motion along the same direction or have a net direction along the motion of our piston. This does not imply that no molecule is moving in the opposite direction or perpendicular directions with respect to the motion that is producing work. It is that the combined motion of the particles in one direction is overwhelmingly high along the direction of the piston movement (expansion or compression). Hence, we need to channel the directions of the molecular motion to produce or acquire work while random motion is sufficient to produce heat. Both are different forms of the same quantity, energy. Heat and work have the same units but the organization of matter in these manifestations is quite different. Work has some component of ordered motions of molecules in a net direction, while random motion is the hallmark of heat.

9.8 Applications in daily Life

Chemical, electrochemical, biochemical, photochemical, the pressure-the volume, mechanical, and other forms of work are all different but share the common characteristic of directed motion. When a bird flies or when we take a walk, for that matter, biological work is being produced in the surroundings. Planes, trains, and automobiles depend on work to function. Similarly, we can also quickly point out the utility of heat in heating or cooling objects, air conditioning, power generation, transportation, and other situations. Thus, these two quantities are intertwined in our civilization, as well as in nature.

9.9 Key points

1. Heat is an algebraic quantity, appears at the boundary, during a process, and is equal to the mass of water required to raise the temperature by one kelvin.
2. Work is an algebraic quantity, it appears at the boundary, during a process, and is equivalent to the masses raised through certain heights in the surroundings, in the earth's gravitational field. The definitions of reversible cyclic and irreversible cyclic processes are important for thermodynamic evaluations.
3. In a cyclic reversible process, the value of W_{cycle} is zero, because of item 10 above.

9.10 Key terms and units

Heat and work have the units of energy, ergs, joules, calories, etc., Specific heat has the units of J/(kg K). Work also has the units of energy, and therefore, we can use the same units for work and heat.

$q = -(T_2 - T_1)\,m\,S$ $w = -p_{ext}\left(V_{final} - V_{initial}\right) = -p_{ext}\,\Delta V$ $dw = -p_{ext}\,dV$ $W = -p_{opp}\,(V_2 - V_1)$

$W_{all} = -n\,R\,T\ln\left(\frac{V_2}{V_1}\right)$ $W_{all} = -n\,R\,T\ln\left(\frac{V_2}{V_1}\right)$

9.11 Self Reflection

1. Plot work as a function of gas the pressure, during a reversible expansion followed by a reversible compression.
2. Plot the same as in problem 1, if the forward and reverse processes are irreversible.
3. Given the space of your dorm room, identify different examples of work of compression or expansion, and discuss if they are reversible or irreversible.
4. What reversible processes are happening on this planet, if the planet earth with its entire atmosphere is considered as your system or list what irreversible processes are happening in this system?
5. In the space of your car, identify several works of expansion and compression as the car burns gasoline.
6. Compare and contrast the two forms of energy, heat and work.

9.12 Further Reading

1. Physical Chemistry by Castellan, 3rd Edition 1967
2. https://ocw.mit.edu/courses/chemistry/5-60-thermodynamics-kinetics-spring-2008/video-lectures/lecture-2-work-heat-first-law/
3. https://ocw.mit.edu/high-school/physics/exam-prep/kinetic-theory-thermodynamics/laws-of-thermodynamics/8_01t_fall_2004_w13d2_class_32.pdf

9.13 Self Tests

1. The temperature of a system of a large beaker of water decreases after bringing it in contact with a large block of ice in its surroundings. The sign of "q" for this process would be:

   a. positive

   b. negative

   c. zero

   d. not enough information

   e. none of the above

2. When a steam engine (system) is pushes a car up the hill, the work that appears at the boundary is,

   a. negative

   b. positive

c. zero

d. infinity

e. none of the above

3. Heat is equal to

a. the temperature in Kelvin

b. mass of water required to raise or lower the temperature by 1 K during a process

c. the temperature in Celsius multiplied by mass

d. the change in temperature multiplied by mass of water

e. none of the above

4. A gas of constant mass, expands at constant temperature to a final volume of 17 liters against an external pressure of 3 atm with work of – 21 atm L appearing at the boundary during the process. The initial volume of the gas is,

a. 24 L

b. 10 L

c. 7 L

d. none of the above

5. If a constant mass of gas in a cylinder decreases in volume during a process, the sign of the work that appears at the boundary (piston) is,

a. positive

b. negative

c. zero

d. infinity

e. none of the above

6. The following is the correct expression for heat

a. $\mathrm{q} = (\mathrm{T}_2 - \mathrm{T}_1)\ \mathrm{m\ S}$

b. $\mathrm{q} = -\ (\mathrm{T}_1 - \mathrm{T}_2)\ \mathrm{m\ S}$

c. $\mathrm{q} = -\ (\mathrm{T}_2 - \mathrm{T}_1)\ \mathrm{S}$

d. $\mathrm{q} = -\ (\mathrm{T}_2 - \mathrm{T}_1)\ \mathrm{m\ S}$

e. none of the above

7. The following is the correct expression for work

a. $\mathrm{w} = -\ p_{ext}\ (V_{final} - V_{initial})$

b. $\mathrm{w} = -\ p_{ext}\ (V_{final} - V_{initial}) +\ p_{ext}\ \Delta V$

c. $\mathrm{w} = -\ p_{ext}\ (V_{final} - V_{initial}) -\ p_{ext}\ \Delta V$

d. $\mathrm{w} = -\ p_{ext}\ (V_{final} - V_{initial})/-\ p_{ext}\ \Delta V$

e. none of the above

8. Work may be understood as due to

a. collective, resultant motion of gas particles

b. flow of gas particles

c. coordinated rotation of gas particles

d. condensation of particles

e. none of the above

9. Heat may be understood as due to

a. ordered motion of gas particles

b. flow of gas particles

c. random motion of gas particles

d. condensation of particles

e. none of the above

10. Which of the following is correct?

a. heat is produced but not destroyed

b. heat is always a positive quantity

c. heat is always a negative quantity

d. heat can be positive or negative

e. none of the above

11. Which of the following is true?

a. work is not a path function

b. work produced at the boundary depends on the path

c. work is a state function

d. work produced at the boundary during a process depends on the path

12. During the adiabatic process, what is the work done?

a. $q=0$

b. 0

c. ΔH

d. $- \Delta U$

e. none of the above

13. An ideal gas was allowed to expand into vacuum at constant temperature, what is the heat that enters the system?

a. 0

b. >0

c. <0

d. Infinity

e. none of the above

14. What is the work done during the one-step isothermal expansion of a gas against constant external pressure (p_{ex})?

a. - p_{ex} x Change in Volume

b. p_{ex} x Change in Volume

c. =0

d. Unknown

e. none of these

15. How is the change in the internal energy of an ideal gas due to adiabatic reversible expansion expressed?

a. -pdV

b. dV/p

c. (nRT/V)dV

d. 0

e. none of these

16. How is the work done during a reversible isothermal expansion of an ideal gas (W_{rev}) related to the corresponding change during an irreversible expansion (W_{irr})?

a. $W_{rev} > W_{irr}$

b. $W_{rev} = W_{irr}$

c. $W_{rev} < W_{irr}$

d. $W_{irr} = 0$

e. none of these

17. An expression for single step, irreversible, isothermal, compression work is

a. $W = -p\,(V_1 - V_2)$

b. $W = p_{opp}\,(V_1 - V_2)$

c. $W = -\,p_{opp}\,(V_2 - V_1)$

d. $W = p_{opp}\,(V_1 - V_2)$

e. none of these

18. The expression for isothermal reversible compression is

a. $W = -\,n\,R\,T\ln(V_2/V_1)$

b. $W = n\,R\,T\ln(V_1/V_2)$

c. $W = -\,n\,R\,T\ln(V_1/V_2)$

d. $W = -\,R\,T\ln(V_1/V_2)$

e. none of these

19. The expression for isothermal reversible expansion is

a. $W = -\,n\,R\,T\ln(V_2/V_1)$

b. $W = n\,R\,T\ln(V_1/V_2)$

c. $W = -\,n\,R\,T\ln(V_1/V_2)$

d. $W = -\,R\,T\ln(V_1/V_2)$

e. none of these

20. The expression for isothermal, single step cyclic expansion followed by compression is

a. $W_{cycle} = (V_2 - V_1)(p_{compression} + p_{expansion})$

b. $W_{cycle} = (V_2 - V_1)(p_{compression} - p_{expansion})$

c. $W_{cycle} = -(V_2 - V_1)(p_{compression} - p_{expansion})$

d. $W_{cycle} = (V_1 - V_2)(p_{compression} - p_{expansion})$

e. none of these

21. The total work done by a reversible cycle is

a. non zero

b. zero

c. >0

d.<0

e. none of these

22. The work done when 1 mol of a gas expands reversibly from an initial volume of 1 liter to a final volume of 2 liters at 300 K is

a. nR 200 K ln (2)

b.- nR 200 K ln (2)

c. nR 200 K ln (1)

d. nR 200 K ln (2)

e. none of these

9.14 Self Tests Key

1. a, 2. a, 3. a, 4. a, 5. c, 6. e, 7. c, 8.a, 9. b, 10. b, 11. e, 12. a, 13. a, 14. a, 15. a, 16. c, 17. e, 18. c, 19.a, 20. b, 21. b, 22. e

9.15 Problems

1. A gas of constant mass expands at a constant temperature to a final volume of 17 liters against an external pressure of 3 atm while work of – 21 atm L appears at the boundary during the process. What is the initial volume of the gas? (Ans. 10 L)
2. What is the work done when a gas expands from 5 to 15 L under constant temperature and constant external pressure of 1 atm? (Ans. -10 atm L)
3. When a reaction took place in the calorimeter, the temperature of the water surrounding the calorimeter rose by 0.255 ˚C. If the mass of calorimeter is negligible when compared to the mass of water surrounding it (1.1 kg), what is the heat released during the reaction? (Ans. 1.173 kJ)
4. Burning of 1.2 g of sugar in a calorimeter of mass 100 g and specific heat of 4000 J/kg.K surrounded by water of 500 g indicated an increase in the temperature of 0.555 ˚C. What is the heat released per g of sugar burned or its food calories? (Ans. 1152 J/g or 1.152 food cal/g)
5. On a hot day, a granite wall of 1100 kg is heated from 50 ˚F to 110 ˚F by the sun and surrounding air. What is the heat stored in the stones of the wall? (Specific heat of granite is 794 J/kg.K) (Ans. 29.1 MJ)
6. Large cities are known to form large heat islands where the heat absorbed during the day is radiated back into atmosphere at night, raising overall temperature of the region. One estimate puts the total mass of all buildings, roads, sidewalks, bridges, cars and other inanimate objects of the Manhattan Island of New York City to be about 250 billion pounds. Using an estimated specific heat of around 900 J/kg.K, estimate the amount of heat stored in Manhattan when its temperature rises by 20 ˚F during a summer day. (Ans. 1.134×10^{15} J)
7. On a hot day, the sun warms up the ground which in turn heats the air above in the atmosphere. Consider one square km area of the ground and a height of 1 km atmosphere with approximate

uniform pressure of 1 atm. What is the work done when the air expands in this volume on heating by sun through 10 ˚C? (Ans. -3.45x10^{13} J)

8. What is the work done when air expands as an ideal gas from 10 L and 3 atm at 300 K into vaccum? (Ans. 0 J)
9. In an internal combustion engine of a typical passenger car, the hot gases expand from an initial pressure of 120 bar to a final pressure of 20 bar, final volume of 250 cc at 700 ˚C. If the load on the piston (diameter of 100 cm^2) is around 250 kg, and if the gas temperature does not change during the expansion, what is the work done when the gases expand fully as the piston moves up? (Ans. 85.7 MJ)
10. Calculate the work done in J, when 1 mol of gas expands reversibly from an initial volume of 1 liter to a final volume of 2 liters at 300 K. (Ans. -1729 J)
11. Calculate the work of an irreversible cycle of isothermal expansion of 0.08 moles of an ideal gas from 1 L to a final state of 2 L and 1 atm, against an external pressure of 1 atm followed by isothermal compression by minimum pressure required to compress it back to the initial state. (Ans. 101.325 J)
12. Calculate the work done in a reversible cycle connecting the initial and final states of problem 11. (Ans 0 J)

Chapter 10. Internal Energy and The First Law

After completing this chapter, you will be able to:

- Recognize the first law of thermodynamics.
- Examine the dependence of the internal energy on the temperature, the volume, and the heat capacity under constant volume conditions.
- Familiarize with Joule's expansion experiment.
- Recognize enthalpy while examining the internal energy as a function of pressure.

Goals

- Analyze the first law of thermodynamics and state it in terms of internal energy, work and heat.
- Define and analyze a new state function, the internal energy (U).
- Synthesize an equation relating the change in U with respect to changes in the volume and temperature.
- Show that U and heat associated with constant volume processes are state functions.
- Quantify the work of gas expansion into vaccum and analyze Joule's experiment.

10.1 Why Study this?

The first law of thermodynamics is one of the most celebrated laws of science, and it simply states that the change in the internal energy of a system is the sum of heat withdrawn from the surroundings and the work produced. It is also the law of conservation of energy. Numerous attempts were made to construct perpetual motion machines with the hopes of breaking this law, without success. The law of conservation of energy is a universal law that governs the energy transformations we experience daily. The law is unbreakable, and this challenge fueled much of thermodynamics in its infancy, and some experiments that led to testing this law are outlined here as well. During these discussions, we will discover the concepts of internal energy and subsequently, enthalpy. A rigorous definition of the first law is critical for continued discussions of thermodynamics of chemical and physical processes, with the ultimate goal of learning why do chemical reactions occur? What characteristic features define if a chemical reaction will occur or not? Thus, this material is important for thermodynamic studies of chemical systems. The corresponding mathematical relations provide tangible insight into the nature of the ideal gas and indicate how real gases deviate from ideal behavior.

10.2 Internal Energy (U)

We will construct a cyclic process and discover a property of a system that does not depend on the path but only on the initial and final states, and this discovery will lead us to the first law of thermodynamics. Our daily experience is that the work produced in the surroundings by a heat engine is equal to the heat withdrawn from the surroundings. At the beginning of the industrial revolution, steam engines powered most of the industrial needs of automation. In a typical steam engine, a certain amount of fuel (coal) is burned, and part of the heat released during the oxidation of coal to carbon dioxide is used to produce steam from water. The steam thus produced is further heated to increase its pressure and high-pressure steam is used to push the piston in the steam box, which turns the wheel of the steam engine. So, a certain amount of heat from the surroundings is used by the system (engine) to produce a certain amount of work in the surroundings (masses are raised) and the cyclic process continued. Each time, the engine will withdraw a certain amount of heat from the surroundings and produce a certain amount of work in the surroundings, in a cyclic process. The engine could not use all the heat to produce work and hence, it released unused heat back into the surroundings. We express this mathematically in the following equation, where an infinitesimal amount of work (dw) is produced in the surroundings by the engine, where it has utilized an infinitesimal amount of heat (dq) from the surroundings. The steam engine is no longer in use in most parts of the world, but it is now replaced almost entirely by the internal combustion engine, where certain amount of heat from burning the fuel is used to produce mechanical work but the same arguments apply here too.

Since heat is acquired from the surroundings or generated internally by these engines, it has a positive sign, and work has a negative sign because masses are raised in the surroundings. We assume that the heat utilized by the engine and the work produced are exactly equal, and any heat that is not converted to work is released into the surroundings. Then, we can write for a cyclic process of the engine that these are equal.

$$\oint dq = -\oint dw$$

The cyclic integrals are used to denote the cyclic process, where the engine cycles between the initial and the final states, as many times as we desire (Figure 10.1). We have the initial state 1 from where the system travels along some path in the forward direction, reaches the final state 2, and then returns to the initial state after traveling along a different path, under certain other conditions. The paths are not defined exactly, and that is not essential for our discussion. We recognize that as the system cycles between the two states 1 and 2, it uses certain dq and produces certain dw during each infinitesimal step of the cycle. We assume that the work produced in the surroundings equal to the heat utilized and test this assumption, very soon.

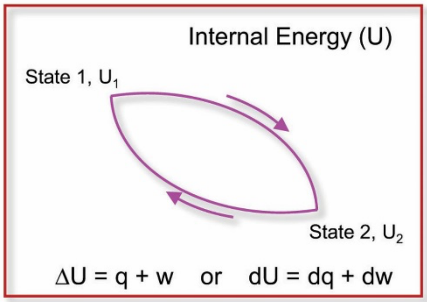

Figure 10.1 Cyclic path for work produced in the surroundings and heat withdrawn by the system, while operating between the initial and final states. Only the status of the system, but not that of the surroundings, is shown.

We rearrange the above equation to write the sum of the two cyclic integrals as equal to zero, as below.

$$\oint dq + \oint dw = \oint d(q + w) = 0$$

If we sum the small changes in q over all the intervals of the forward and reverse paths and add to the sum of all the corresponding small changes in w, over the whole cycle, the sum is equal to zero. Therefore, we conclude that we must have a new property of the system which does not change as the engine performs this cyclic process, which means that this sum is a state function. Therefore, (dq + dw) must be a state function. We recognize that there is a new kind of property of the system that is equal to the sum of the path functions, q, and w. For the sake of convenience, we write this sum with a new variable, U, and write these developments with the following equations.

$$\oint dU = \oint dq + \oint dw$$

$$dU = dq + dw$$

This is the first law of thermodynamics, but we will explore this further, in a bit. We use U as the symbol for internal energy, and dU is the infinitesimal change in the internal energy which is equal to the sum of the infinitesimal changes in q and w. Even though both q and w are path functions on their own, their sum is a state function. This equality also applies to any other cyclic transformation because U is a state function, and thus, does not depend on the path. Thus, we can write the above equation for any cyclic process. The above formulations are expressions for the first law of thermodynamics, as discussed below.

Previously, we calculated the internal energy of an ideal gas to be all its kinetic energy, (3/2) nRT with (1/2) nRT for each degree of freedom. Since it is a particle of zero volume, it has only translational degrees of freedom, along the X-, Y- and the Z-coordinates, thus 3*(1/2)nRT. When we heat an ideal gas through certain temperature, $\Delta U = (3/2)nR(T_2 - T_1)$.

10.3 The First Law of Thermodynamics

The first law is also the law of conservation of energy, and this is because the work and heat terms must be exactly equal to the change in the internal energy, there can't be any compromise. It is written mathematically using the above expression. We recognize in Figure 10.1 that U_1 is the internal energy of the system in the initial state 1 and U_2 is the internal energy of the system in the final state 2, and dU is the change in energy as the system travels along any path by an infinitesimal amount, then dU is given as the sum of the infinitesimal change of q, dq plus the infinitesimal change in w, dw. By integrating the expression on both sides using the corresponding initial and final states, we get the following expressions.

$$\int_1^2 dU = \int_1^2 dq + \int_1^2 dw$$

$$U_2 - U_1 = \Delta U = q + W$$

$$\Delta U = q + w$$

$$\int_{Cycle} dU = 0$$

The change in U when the system travels along any path from the initial state to the final state (ΔU) was obtained by integrating this equation and given as equal to q + w. Note that q and w are path functions and hence, we denote the corresponding integrated values as q and w, respectively. For this reason, we do not use the delta symbol for these quantities and these path functions have different values for different paths. We can write ΔU as the value of the integral because U is a state function and not a path function. Then, ΔU equals the difference between U_2 and U_1 and equals q plus w. The first law is a major conservation law and can't be broken, under any of the conditions that we know so far.

Example 10.1

Calculate ΔU when a gas is allowed to expand adiabatically from an initial volume of 5 liters to a final volume of 15 liters against an external pressure of 1 atm, at constant temperature and mass.

U = q + w, q = 0; ΔU = w = - external the pressure x change in the volume

= - p_{ext} (V_{final} – $V_{initial}$) = - 1 atm x 10 L = - 15 atm L

Thus, the new state function U is called internal energy, and internal energy is conserved during any process. The first law of thermodynamics has been extensively tested over centuries, in attempts of constructing perpetual motion machines, and all of which have failed, lending support to the establishment of the energy conservation law or the first law of thermodynamics. The definition of internal energy is itself the first law of thermodynamics which clearly states that the internal energy can neither be created nor destroyed during any transformation, only one form is converted to another. Thus, the assumption we made earlier that the heat utilized is equal to the work produced must be correct and that followed the definition of internal energy. Thus, the proof for internal energy to be state function and the derivation of the first law must also be correct.

Example 10.2

Explain how the first law of thermodynamics is obeyed by nuclear fission or fusion reactions?

The energy released during the thermonuclear reactions or nuclear fusion also follows this law due to Einstein's mass-energy equivalence. That is mass is being converted into energy and hence, the conservation law is extended to mass-energy equivalence and still can't be broken. When a chemical reaction occurs, heat may be released or absorbed, and this energy is also related to the accompanying change in the mass of the products/reactants. Although the mass change during a chemical reaction is beyond our ability to measure, being too small for all current methods of measurements. The fact is that the energy is derived by converting the corresponding mass as defined by the Einstein's mass-energy equivalence. Thus, the first law itself is modified to account for mass-energy equivalence as the conservation of mass and energy, as equivalents.

In the case of pV work, heat which is a form of energy is being converted to work, another form of energy. The amount of heat converted is exactly equal to the work produced and hence, energy conservation is achieved. However, note that none of the machines can completely convert the heat they withdraw from surroundings into work, some part of the heat is converted to work and the remaining is given back to the surroundings. Thus, the above law exactly accounts for the amount of heat utilized by the engine to produce work, not the amount of heat withdrawn, and a clear distinction needs to be made between these two. While only a portion of heat can be converted into work, all the work can be converted completely into heat. This is a distinction for heat. Any form of energy can be converted into heat completely, but the converse is not true. More of these aspects will be discussed in later chapters.

Example 10.3

Apply the first law of thermodynamics for making a cup of coffee in the morning. Use your imagination to choose the system and the process, appropriately.

We define the coffee cup with liquid water filled two-thirds the way with the boundary of the liquid separating the surroundings from the system, as in the previous chapter. We heat the coffee in the microwave and transfer some energy from the surroundings into the system. The electrical energy from the utilities company is used to produce microwaves, some of which are absorbed by the water, and the temperature rises. Total energy drawn from the utilities should be the sum of the heat produced while converting it into microwaves, the energy absorbed by the water, and the energy of the unused microwaves dissipated into the surroundings. Not a bit of energy is wasted (unused) and it is used for something, raising the temperature of the system and the surroundings. Energy can neither be created nor destroyed and hence, we did not consume the energy from the utilities, we just converted it into other forms. Is it still advisable to pay the utility bill at the end of the month, because energy is not being consumed?

In summary, a new thermodynamic property has been discovered by constructing a cyclic transformation, and based on extensive experimental observations, we conclude that the sum of heat and work changes in a cyclic transformation is zero. We will extend our discussions of the first law in the subsequent sections as well. Next, we will examine U as a function of other variables of the system.

10.4 U as a function of T and V

We examine the properties of internal energy, the newly discovered state function, in terms of its dependence on the temperature and the volume of our system. That is, we ask how does U depends on T and V? The change in the internal energy with respect to these two properties is written by using the exact differentials. The exact differential of y in terms of x and z are shown below, where the first term on the right accounts for changes in y due to x when z is kept constant, and the second term corresponds to changes in y due to z while x is being kept constant. The sum of these two changes accounts for the net change in y due to x and z. Analogously, we write infinitesimal change in U is equal to the sum of two terms, one depends on the temperature and the other depends on the volume.

$$\mathrm{dy} = \left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial y}{\partial z}\right)_x dz$$

$$\mathrm{dU} = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

The first term on the right of the second equation is the rate of change of U with respect to the temperature multiplied by an infinitesimal change in the temperature. This term gives us the total contribution of the temperature to dU. As we discussed in the introductory math, the differential is the rate of change and when we multiply this with the width of the change (dT), we get the total change, which is solely due to the temperature.

Similarly, the second term on the right accounts for the rate of change of U with respect to V multiplied by the infinitesimal change in the volume, and this term accounts for all the contributions to U with respect to V. Notice that the first term is estimated when the volume is kept constant, so that all changes in U are solely due to T during this step, and in the second term we are keeping T constant so that all changes in U are solely due to V during this step. Thus, the net change in U is given as the sum of these two terms. These are the typical properties of exact differentials, and we exploit this situation to write U in terms of the two variables, T, and V. This process can be carried out with any number of variables, but T and V will be sufficient for our current discussions. Figure 10.2A, B, C show some examples of plots of the terms as exact differentials.

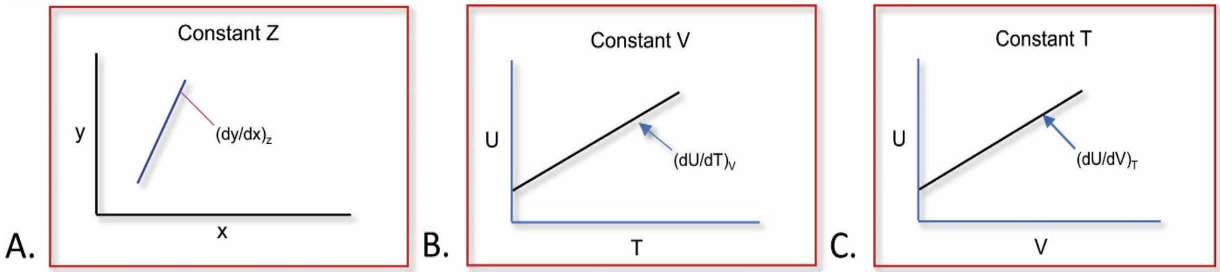

Figure 10.2 The first derivative of y with respect to x at constant z, is shown in the first panel A, where the tangent has the slope of the first derivative at a randomly chosen point. Along these lines, the first derivative of U with respect to T, under constant volume conditions is shown in panel B, while the third panel C, shows the change in U as a function of V, at constant T. The functions of U are taken as linear with positive slopes for the sake of argument, but they will be investigated further, below.

The first panel of Figure 10.2 shows a plot of y (which is a function of x and z) with respect to x at constant z, and a tangent to the function has been drawn at an arbitrary point which is of interest, for our argument. The slope of the line is the first derivative of y with respect to x, but it is being evaluated while z is being kept constant. Therefore, z has nothing to contribute toward the change in y, and all changes in y are solely due to changes in x. This contribution of x is given by the rate of change of y with x multiplied by the change in x, or dx.

Example 10.4

What is the rate of change of any property, explain in simple terms?

For example, you're traveling in your car on route 84E at 55 mph, then 55 miles per hour is the rate of change of your position on the highway. Now, if you were to t1avel for five minutes at this uniform speed, then we can calculate the distance traveled during this interval as, speed multiplied by the time interval of five minutes. So, the first derivative in this example is analogous to the speed, and dT is analogous to the time interval 5 minutes traveled, except that it is not infinitesimal change in time, some minor deviation but the argument still holds. Thus, the total distance traveled by your car in that time interval is obtained by the first derivative of distance with respect to time (speed) multiplied by the time interval (5 minutes). We apply the same argument to get change in U with respect to any variable of interest. We also notice that the units work out correctly for this type of analysis.

Along these lines, the second panel of Figure 10.2 shows the first derivatives of U with respect to T, under constant volume conditions. We are plotting U as a function of the temperature, but U is also a function of the volume, but you're holding that constant. In the third panel, we are examining U as a function of V, while holding T constant. The functions of U are taken here as linear with positive slopes, for the sake of argument, but we will examine these in more detail later. Thus, a function of two or more variables such as U can be examined in terms of several different contributions, each while varying a single variable, and keeping all the remaining constant.

Imagine that we have enclosed a gas sample in a cylinder, and we are keeping the pressure constant but allowing both the temperature and the volume to vary by supplying q (Figure 10.3). We will carry out this transformation in two steps. For convenience, the first step being carried out at constant volume and allow the temperature to increase, and during the second step, we hold the temperature constant and allow the volume to increase so that the pressure is restored to the initial pressure of the system. Since U is state property, it does not matter thermodynamically how we travel from our initial state to the final state, and we could use a variety of different paths, but this is one of those that are relevant to the equations we wrote for dU above.

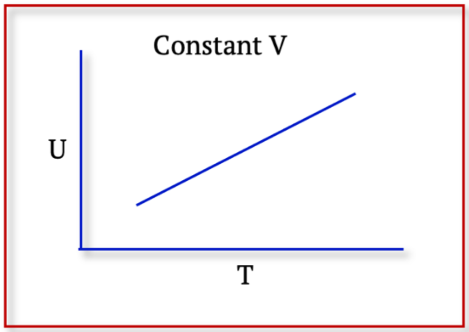

Figure 10.3 The internal energy (U) of a gas sample with respect to a change in the temperature and volume at constant the pressure or vary T at constant p, V; and then vary V at constant p and T, while keeping the gas mass constant. Since U is a state function, we could choose any path, but this is analogous to the mathematical expressions that we wrote for U, as a function of T and V, at constant pressure.

10.5 U as a Function of T, Isochoric Process

We will examine each of the above scenarios, separately, where we hold one variable constant and vary the other. Here, we will hold the volume constant, while examining how U depends on the temperature of the system. Since we are keeping the volume as constant, dV = 0, and hence, the second term in the exact differential of U above drops out, and we have U as a function of T alone, as given below.

$$\mathrm{dU} = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

$$\mathrm{dU} = \left(\frac{\partial U}{\partial T}\right)_V dT + 0$$

$$\mathrm{dU} = C_V\, dT$$

The change in internal energy at constant volume is entirely due to a change in the temperature or the change in the kinetic energy of the system. We recall, we have postulated that internal energy is the kinetic energy for an ideal gas or that it is the sum of the microscopic kinetic and potential energies of a real gas, and now we confirm this assertion. Thus, we examine this dependence, and the slope of the function of U at constant the volume conditions is the first derivative of U with respect to T at constant V. We call this derivative as the heat capacity of the system (C_V) under constant the volume conditions (Figure 10.4).

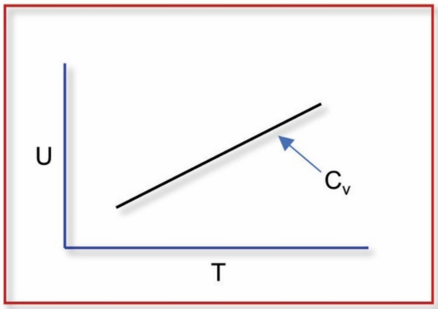

Figure 10.4 U as a function of T, at constant the volume, and the slope of the plot is the first derivative of U with respect to T, at constant the volume, which is defined as the heat capacity of the system under constant volume conditions (C_V). We chose a linear function with a positive constant slope (ideal gas) but it need not be linear or constant for real substances, but the slope is positive for all substances.

Under these conditions, all the heat supplied to the system to raise its temperature is being added to the kinetic/potential energy of the gas particles, and an increase in the kinetic/potential energy is a measure of its heat capacity or capacity to store heat energy in the system. No work is performed here because dV = 0. This capacity to store heat under constant volume conditions is further discussed in the next section.

10.5.1 Heat capacity at constant V

In the above equation, dU equals C_V dT where Cv is the first derivative of U with respect to T at constant volume, and this was defined above as the heat capacity under constant volume (C_v) conditions. This is because, we are heating the sample and measuring the increase in the temperature of the system, while holding the volume constant, but allowing the pressure to increase. Thus, the system takes the heat, the kinetic energy of the gas particles increases, and this is manifested as an increase in the temperature. But different substances increase their temperature at different extents for the same amount of heat supplied. Thus, heat capacity defined as above is an important intrinsic property of the system.

We can also look at it as the contribution of T to U which is given by the product of the heat capacity under constant volume conditions multiplied by the change in the temperature. Since this is a constant volume process, the change in the internal energy of the system is equal to the rate of change of U with respect to T at constant the volume, which is the heat capacity of the system at constant the volume, multiplied by the change in the temperature. By rearranging the terms, we see that the heat capacity is the rate of change of U with respect to T, or the slope of the plot in Figure 10.4, as we defined earlier. Explicitly, the rate of change of U with respect to T at constant volume is the heat capacity of the system under constant volume conditions, as explained above. This has practical implications.

$$\mathrm{dU} = C_V\, dT$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

Example 10.5

Let us take a practical example of heating your house during the winter months in North America. We are heating the house and assume that the house and its contents do not change the volume significantly during the heating, over the small temperature interval, say 55 ˚F to 70 ˚F, and tightly sealed. We supply a certain amount of heat to raise the temperature to a comfortable level and the amount of heat to accomplish this depends upon the construction of the house. If the house is built with stone, then it takes a lot more heat than if it is built with wood. We know that the heat capacity of wood is lower than that of stone. Thus, your heating bills depend on the materials used to build the house. Similarly, it depends on the furniture used, the interior wall materials, the roof material, etc., Thus, heat capacity plays a very important role in our daily lives, which we may not have yet recognized. In the laboratory, the heat capacity is connected to the heat of reaction, the mechanism of solvation, and many other intricate properties of the molecules we study.

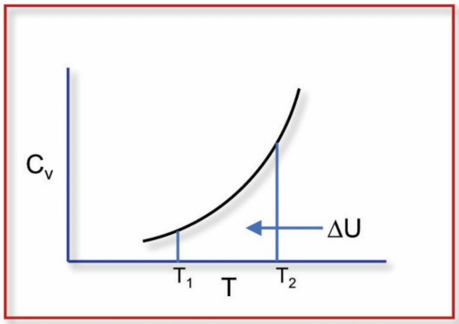

Figure 10.5 The heat capacity at constant volume can also be a function of the temperature, unless C_v is constant for a given substance, such as an ideal gas.

Table 10.1 Values of molar heat capacities at constant volume and the pressure for a few substances

Symbol	*Air*	*Ar*	*CO_2*	*H_2O*	*N_2*	*O_2*
Cv/ (J mol^{-1} K^{-1})	20.6	12.47	28.6	74.3	20.8	21.0
Cp/ (J mol^{-1} K^{-1})	29.2	20.79	36.94	75.33	29.12	29.83

We also recognize that C_v could also depend on the temperature, itself. In other words, a plot of C_v vs T for our system could be nonlinear (Figure 10.5), requiring more heat or less heat as we continue to heat the system. For an ideal gas, C_v is a constant, but this is not the case for all substances. For example, when we heat the oven to bake bread, we notice that the initial rise in the temperature to around 200˚F is rather quick and then it takes much longer to reach 400 ˚F. This could be because C_v is changing with the temperature, or it could be that the oven leaks more heat at higher temperatures (Newton's law of cooling) than at lower temperatures. Nevertheless, heat capacity plays a very important role in cooking, heating, baking, and other things as well. As the air is filled with more CO_2 in the atmosphere due to various sources on our planet, the heat capacity of air increases, storing more heat in the atmosphere than normal, and hence, contributing to climate change, an undeniable fact.

10.5.2 Change in U, during an isochoric process

We will obtain the change in U when we change the temperature, under constant volume conditions (isochoric process). Using the exact differential of U in terms of T and V, and by setting dV = 0, we get $dU = C_v\, dT$. We can integrate this expression between the initial state 1 and the final state 2 if C_v is Independent of the temperature or a constant. Thus, a plot of Cv as a function of the temperature will be a line parallel to the T axis. C_v is a constant for an ideal gas, for example (Figure 9.5, ideal gas). The integration gives us the following result.

$$\Delta \mathrm{U} = \int_1^2 dU = \int_1^2 C_V\, dT = C_V \int_1^2 dT = C_V\,(T_2 - T_1)$$

We assign the temperature of the initial state as T_1 and that of the final state as T_2, and hence, the change in U is given as ΔU equal to the product of C_v and ΔT, written explicitly. Therefore, the internal energy of an ideal gas increases with the temperature, linearly with a constant slope of C_v. If C_v is not a constant, we can integrate the above expression after writing C_v in terms of a function of the temperature, $C_v = (aT + bT^2 + cT^3 + \ldots$ where a, b, c,…. etc., are constants, that is, they do not depend on T). Now, we can integrate the expression, which is now expressed only in terms of the temperature. Thus, we can obtain an expression for U as a function T as shown above.

10.5.3 q_v is a state function

Another insight we glean from the above equation for U, in terms of T at constant V, is that the system does not perform any pV work during the isochoric process. This is because dV = 0, and hence, masses are not raised or lowered in the surroundings and therefore, all the heat supplied to the system is used to raise the temperature of the gas! Using the first law of thermodynamics we show that when w = 0, ΔU = q, for the isochoric process (q_v). Thus, we represent q during the isochoric heating as equal to q_v. That is, heat that is absorbed or released in a constant volume process is exactly equal to ΔU. Thus, for all isochoric processes we have the following expression.

$$\Delta \mathrm{U} = \int_1^2 dU = C_V\,(T_2 - T_1) = q_V$$

Since U is a state function, ΔU is a state function and then q_v should also be a state function. In a manner, like work in a reversible cyclic process which is a state function, we find that q_v is a state function for isochoric heating. Thus, even though heat is normally a path function, in an isochoric process it is a state function, a very important recognition for heat. So, we can write dq_v in the expression for C_v, and this gives a means to directly measure C_v and ΔU by experiments.

$$\frac{dq_V}{dT} = C_V$$

A plot of q_v vs T gives a function whose slope is the heat capacity at constant volume conditions, and we can do such measurements in the laboratory (Figure 10.5). We supply heat to the system under constant volume conditions and measure its temperature changes. From the plot, we determine the slope of the plot at specific temperatures and estimate the corresponding heat capacity values of our system. If the heat capacity is independent of T, then the plot will be a straight line with a constant slope at all points, but if heat capacity is not a constant then the plot will be non-linear, slope varying as we increase the temperature (Figure 10.6). One important practical observation has been that C_v is always greater than zero. That is, we need to supply q to raise the temperature of the system, for all substances. This is another fundamental law, which we will use in a later chapter.

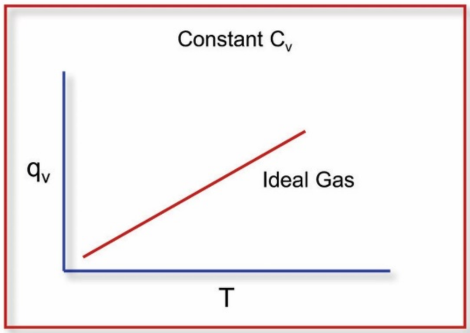

Figure 10.6 The heat supplied in an isochoric process and the corresponding increase in the temperature. If C_v is constant, then the plot is a straight line with a positive slope, but if it is not a constant it will be a curve. Note that $C_v > 0$ for all substances.

Example 10.6

Calculate the heat capacity of a gas as it is heated in a microwave by supplying 100 kcal of heat, under constant volume conditions, from 25 to 35 ˚C. Assume that all the supplied heat is used to heat the gas sample.

$C_v = \Delta U / (T_2-T_1) = (q + w)/(T_2-T_1) = 100$ kcal/(35-25) ˚C = 10 kcal/˚C

10.6 U as a Function of V, Isothermal Process

Using the exact differential of U in terms of T and V, we examine the effect of V on U, when T is kept constant. Since T is a constant, this is an isothermal process. Recall the exact differential of dU and impose the constant temperature condition (dT = 0) to get the following relations.

$$\mathrm{dU} = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

$$\mathrm{dU} = \left(\frac{\partial U}{\partial V}\right)_T dV + 0, \qquad constant\ T$$

The expression tells us that a plot of U vs V will be a function with a slope equation to $(dU/dV)_T$, and the infinitesimal change in U is due to the rate of change of U with respect to V multiplied by dV. If the slope is constant, then we have a linear function, or else it is a curve. It is also possible that the slope could be zero and then the line will be parallel to the volume axis (Figure 10.7).

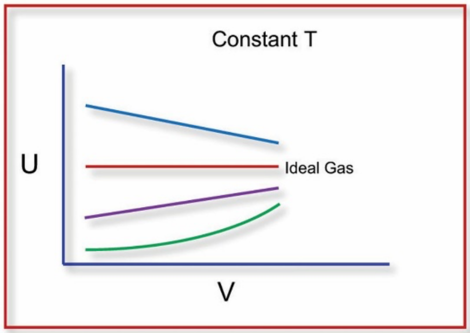

Figure 10.7 Plot of U vs V at constant T, for different gases. The slope is equal to zero (ideal gas, red line), but for real gases it can be positive or negative, constant or variable.

Joule studied how U varies with V, under isothermal conditions. Since the volume is not a constant, the expanding gas could produce work during the process, but if the expansion is into the vacuum, then the opposing pressure is zero ($p_{opp} = 0$), and the work produced is zero even though dV≠0. Then, dw = 0, and by applying the first law of thermodynamics, we conclude that dU = dq. Thus, we need an experiment to determine dq when the gas expands into a vacuum under isothermal conditions to evaluate dU. Joule examined this question by carrying out the expansion of air against vacuum, free expansion, as described below.

10.6.1 Free (Joule) expansion

Joule has conducted a historical experiment to test the gas expansion into the vacuum and the change in the internal energy (dU) of the gas. A container of gas was immersed in a water bath (calorimeter) and half of this container has been separated from the rest via a small valve. One part is filled with air up to 22 bar, and the other half has been evacuated to near zero pressure. After the container has been thermally equilibrated, isothermal conditions, the valve was opened suddenly allowing the gas to expand spontaneously against zero opposing the pressure (free expansion). If there is a change in U, then there should be a change in the temperature of the gas, and the temperature has been monitored after the free expansion (Figure 10.8).

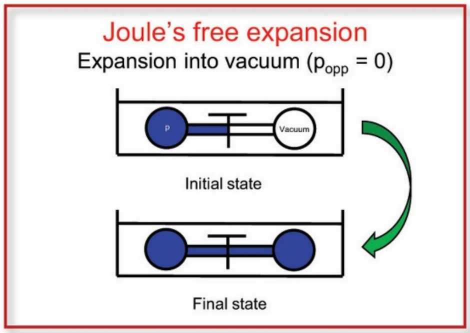

Figure 10.8 Expansion of the gas against vacuum (free expansion) indicated no change in the temperature of the gas. Since the opposing the pressure is zero, w = 0, no the temperature change was noted (ΔT = 0), then dU = 0.

Joule could not find a change in the temperature of the gas, within the experimental error of his apparatus, and concluded that ΔT = 0, dU = 0. The first term in the exact differential drops out but dV ≠ 0, and so we can write the following equations.

$$\mathrm{dU} = \left(\frac{\partial U}{\partial V}\right)_T dV + 0$$

$$dU = 0;\ \left(\frac{\partial U}{\partial V}\right)_T = 0$$

In summary, the free expansion results in w = 0 because there is no opposing pressure for the gas to work against, and there was no change in the temperature during the expansion, and hence, dU = 0. According to the first law, we conclude that q = 0. Therefore, we conclude that the change in internal energy as a function of the volume is zero. However, we now know that for most real gases the change in the temperature for free expansion is not zero and depends on the gas used for the expansion. Joule's conclusion was in error because of the large errors in temperature measurements and the large heat capacity of the calorimeter he used. Only in the case of the ideal gas ΔT = 0 for the free expansion, this is because the intermolecular interactions do not exist in an ideal gas, and no work is performed during the free expansion. But for many real gases ΔT ≠ 0, and when free expansion occurs, work is being done to overcome these interactions, and the temperature of the gas changes after the free expansion, sign, and magnitude of which depends on the gas used. For real gases, the following may apply.

$$\left(\frac{\partial U}{\partial V}\right)_T \neq 0$$

10.7 Molecular Interpretation

The internal energy of an ideal gas is purely kinetic, and more specifically it is the translational energy of the gas particles (1/2 mc^2). This is simply because there are no interparticle interactions in an ideal gas and it has no vibrational or rotational energy because it is a single particle. Thus, all its energy is manifesting as the kinetic energy, the internal energy of the gas, U. Real gases, on the other hand, do have kinetic energy similar to the ideal gas. In addition, real gases also have interparticle interactions and intra-particle interactions, and hence, they do have potential energy. Even the kinetic energy is distributed among all the degrees of freedom, and hence, there are several reservoirs where the internal energy is stored. Thus, various types of motions, as well as potential energy, contribute to the internal energy of a real gas. In later chapters, we will recognize that the kinetic energy of the oscillator is not zero even at 0 K, which is called the zero-point energy. For an ideal gas, though, the internal energy is zero at 0 K and we may recall that we have arrived at this value in the earlier chapters (U = 3/2 RT).

The first law of thermodynamics is a practical law, but it can also be understood in terms of molecular properties because it is the law of conservation of energy. If a certain amount of heat is used to produce work, we are converting disordered motion into directional motion. That is, by simply increasing the temperature, we are increasing the random motion of the gas particles. However, if we allow the system to perform work by pushing a piston up, for example, then the gas particles are directed to move in one resultant direction. They may still be moving randomly but the overall motion of all the particles summed together produces a net motion along the direction of the movement of the piston. Thus, while heat is a manifestation of random motion, we can think of work as directional motion where all the directions of the particles when summed over, gives a non-zero direction for the motion of the particles. Thus, when we supply energy to the gas, part of it is used to increase the overall kinetic energy and potential energy (if allowed) of the gas, and part of it is used to perform work (if allowed). Therefore, the internal energy of the gas will be the sum of its kinetic and potential energy terms and the energy of work. There is no other component of energy, and hence, all the energy is accounted for by these three terms, providing a molecular basis for the law of conservation of energy.

Even chemical reactions are no exception to the law of conservation of energy. When a chemical reaction occurs and heat is liberated or absorbed, the energy is still conserved. This is so because certain amount of mass is destroyed to release the energy as given by Einstein's mass-energy equivalence or certain mass is created when heat is absorbed. However, this change in the mass during a chemical reaction is so small that it is often neglected or can't even be measured in most cases. Thus, the first law is extended to chemical reactions by accommodating the mass-energy equivalence.

The effect of the temperature on the internal energy of the gas is readily understood in terms of the above descriptions of internal energy. As we increase the temperature of the ideal gas, the particles gain kinetic energy and travel at higher and higher speeds, we derived expressions for this, and this increase in kinetic energy is then manifested as an increase in the internal energy of the gas. Similar is the situation with real gases as well, except that some of the heat supplied could also be used to increase the potential energy of the gas, stretching the bonds, or increasing the rotational motion or the vibrational motion. Thus, internal energy increases with the temperature, but the energy is distributed among its various degrees of freedom, in addition to the translational motion.

Molecular description of heat capacity is complicated and has very many contributions, but the treatment we examined here, is a simple one. The heat capacity of a system is due to its ability to store heat, and the greater the degrees of freedom a gas has, the greater will be the heat capacity. If each degree of freedom is a bucket, we have more buckets to store energy with, a greater number of degrees of freedom, and greater heat capacity. Greater the heat capacity slower will be the rise in the temperature of our system. This is because the supplied energy is used to populate a greater number of degrees of freedom in the gas by filling more and more buckets to higher and higher levels. Again, C_v will be the lowest value for an ideal gas as it has only 3 translational degrees of freedom. In solids and liquids, the interparticle interactions contribute significantly to heat capacity, while their translational motion is severely restricted, and their heat capacities are substantially higher than gases.

The effect of the volume on internal energy is not so straightforward to understand. As we hold the temperature constant and raise the volume by allowing it to expand freely into the vacuum, the gas particles are pulled apart further and further. In the case of an ideal gas, which has no interparticle interactions, the temperature of the gas remains the same. However, in the case of real gases, the interparticle and intraparticle interactions contribute to the temperature changes, as the gas expands, depending on the gas being examined.

10.8 Applications in Daily Life

The first law is the foundation stone for our discussions of thermodynamics in real life. The recognition that work can't be produced out of thin air (conservation of energy) took a long and hard path. Finally, we now know that we can produce work at the expense of some other form of energy such as heat, electrical, photochemical, biochemical, or some other form. Thus, this law is all pervasive and our imagination is the only limit in discovering new applications of this law in our daily life and we encourage the reader to reflect on this suggestion. Thus, both in the lab and in life, the first law and internal energy are of extreme importance.

10.9 Key points

1. The first law of thermodynamics states that the work produced in the surroundings is exactly equal to the work withdrawn from the surroundings.
2. The first law is also the law of conservation of energy and states that energy can neither be created nor destroyed. This is true even with the discovery of the God particle.
3. Internal energy is the sum of the kinetic and potential energies of the gas particles and for an ideal gas it is solely the kinetic energy.
4. The interparticle and intraparticle interactions in real gases contribute to the potential energy which is part of the internal energy of real gases.
5. When we heat a gas sample to raise its temperature, at constant volume, the heat energy is used to raise the kinetic and potential energies of the particles. Since the ideal gas has only kinetic energy, all the heat energy is used to raise the kinetic energy only, manifesting as a rise in its temperature.
6. Heat capacity under constant volume conditions is the rate of change of internal energy with the temperature at constant volume.
7. The rate of change of internal energy of an ideal gas, with respect to the volume at a constant temperature, is zero. This is because the ideal gas particles have no interparticle or intraparticle interactions.

10.10 New terms and units

Internal energy, the first law of thermodynamics, the law of conservation of energy, heat capacity under constant volume conditions, and Joule's (free) expansion. The units of internal energy are the same as energy, which we have already discussed in earlier chapters. Unit of heat capacity is simply energy/K or energy/˚C.

$$dU = dq + dw \qquad \left(\frac{\partial U}{\partial V}\right)_T = 0 \qquad \Delta \mathrm{U} = \int_1^2 dU = C_V\,(T_2 - T_1) = q_V$$

10.11 Self Reflection

1. Sketch a plot of the system traveling from an initial state to the final state with changes in the internal energy of the system as a function of the temperature, under constant volume conditions.
2. In the space of your dorm room apply the first law of thermodynamics to the specific process occurring there.
3. Discuss the application of the law of conservation of energy in the situation when you drive the car up a mountain or down the hill.
4. Discuss the applicability of the first law to the operation of a coal-fired power station in the Midwest.
5. Plot a 3D graph of U, V, and T for an ideal gas and compare it with such a plot for a real gas.
6. The molar heat capacities at constant pressure (J/mol K) of few gases are Methane (35.69), CO_2 (36.94), H_2O_{vapor} (75.33), He (20.79), and Ar (20.79). Test the hypothesis that heat capacity is proportional to the total degrees of freedom of a gas.
7. In the space of your dorm room apply the first law of thermodynamics to the specific process occurring there.
8. Compare the nature of internal energy with those of work and heat.

10.12 Further Reading

1. https://ocw.mit.edu/courses/chemistry/5-60-thermodynamics-kinetics-spring-2008/video-lectures/lecture-2-work-heat-first-law/
2. https://ocw.mit.edu/high-school/physics/exam-prep/kinetic-theory-thermodynamics/laws-of-thermodynamics/

10.13 Self Tests

1. An ideal gas (1 mol, 1 atm) is heated from 290 to 295 K under constant pressure conditions. What is the heat capacity at constant volume?

   a. $\ln 0.5/\ln(290/295)$

   b. $\ln(290/295)/\ln 0.5$

   c. 0

   d. 1

   e. None of these

2. What is the change in internal energy when an ideal gas is heated through dT at constant volume?

   a. $C_v dT$

   b. $-C_v dT$

   c. C_v/dT

   d. dT/C_v

   e. none of these

3. Which of the following is the correct expression for heat capacity (C_v) in an isochoric process?

   a. $C_v(T_2-T_1)$

   b. dq_v/dT

   c. $-dq_v/dT$

   d. $(\Delta T/\Delta p)$

   e. none of the above

4. Which of the following is the correct expression for the change in internal energy in an isothermal process?

   a. $(dU/dV)_T$

   b. $C_v dT$

   c. dq_v/dT

   d. $(dU/dV)_V$

5. The work that appears at the boundary of a system during an adiabatic process is

   a. equal to the change in the internal energy of the system

   b. equal to the heat absorbed

   c. equal to the change in the heat

   d. equal to zero

   e. none of these

6. By heating an ideal gas the heat energy is used to

   a. raise the kinetic and potential energies of the gas particles

b. raise potential energies of the gas particles

c. raise the kinetic energies of the gas particles

d. use to overcome the intermolecular forces

e. none of these

7. For an ideal gas (dU/dV)T = 0 because ideal gas particles

a. have more interparticle interactions than intraparticle interactions

b. have more intraparticle interactions than interparticle interactions

c. have no intraparticle interactions or interparticle interactions

d. have only intraparticle interactions

8. The change in temperature during the free expansion of ________ gas is equal to zero.

a. real

b. ideal

c. either real or ideal

d. diatomic

e. van der Waal's

9. Which of the following is the correct expression for the heat capacity under constant volume conditions?

a. $\frac{dU_V}{dT} = C_V$

b. $\frac{dq_V}{dT} = C_V$

c. $\frac{dp_V}{dT} = C_V$

d. none of the above

10. As a real gas expands adiabatically its temperature

a. increases due to interparticle interactions

b. does not change

c. decreases due to interparticle interactions

d. decreases

e. none of the above

11. As an ideal gas expands adiabatically its temperature

a. increases due to interparticle interactions

b. does not change

c. decreases due to interparticle interactions

d. decreases

e. none of the above

12. As a real gas expands adiabatically, its internal energy

a. increases due to interparticle interactions

b. does not change

c. decreases due to work that appears at the surroundings

d. decreases

e. none of the above

13. The expression for the first law of thermodynamics is

a. dU = dq - dw

b. dU + dq = dw

c. dU-dq = dw

d. dU + dw = dq

e. none of the above

14. Change in ΔU for isochoric heating of an ideal gas is

a. $\Delta \mathrm{U} = C_V\ (T_2 - T_1)$

b. does not change

c. zero

d. $\Delta \mathrm{U} = C_V\ (T_1 - T_2)$

e. none of the above

15. At constant temperature, the value of $\left(\frac{\partial U}{\partial T}\right)_V dT$

a. increases due to interparticle interactions

b. is zero

c. decreases due to interparticle interactions

d. decreases

e. none of the above

16. Plot of U vs V for an ideal gas at constant temperature is

a. exponential

b. linear with no slope

c. linear with negative slope

d. linear with positive slope

e. none of the above

17. For an ideal gas, the value of $\left(\frac{\partial U}{\partial V}\right)_T$

a. increases due to interparticle interactions

b. >0 and does not change

c. decreases due to interparticle interactions

d. decreases

e. none of the above

18. For a real gas, the value of $\left(\frac{\partial U}{\partial V}\right)_T$

a. 0

b. >0 and does not change

c. <0 or >0 but not equal to zero

d. >1

e. none of the above

19. For a real gas, the value of U is

a. (5/2) RT

b. ½ RT

c. RT

d. 2 RT

e. none of the above

20. For an idea gas, the value of $\left(\frac{\partial U}{\partial V}\right)_T$

a. (3/2) RT

b. 3 RT

c. RT

d. 2 RT

e. none of the above

10.14 Self Tests Key

1.e, 2. a, 3.b, 4.a, 5.a, 6.c, 7.c, 8.b, 9.b, 10.d, 11.d, 12.c,13.c, 14.a, 15.b, 16.b, 17e, 18. e, 19.e, 20.a

10.15 Problems

1. An ideal gas (1 mol, 1 atm) was heated from 290 to 295 K in an isochoric process. What is the heat absorbed at constant volume? (Ans. 62.36 J)
2. A gas sample of 1 mol was heated under constant pressure of 1 atm from 300 to 400 K. What is the change in the internal energy, q and w during this process? (Ans. 1247 J, 1255 J, and -8.2 J)
3. An ideal gas was allowed to expand through a pin hole into vacuum at constant temperature of 300 K from an initial pressure of 1 atm and initial volume of 10 L. What are ΔU, q and w accompanying this process? (Ans. 0 J, 0 J, and 0 J)
4. Hypothetically, a hydrogen car can burn hydrogen and oxygen and produce work in a cylinder similar to that of an internal combustion engine. If 1 mole of hydrogen is completely converted in just enough pure oxygen with a catalyst into water at room temperature (300 K), what is the work produced in a one-step expansion against the atmospheric pressure? (heat of combustion of hydrogen = 286 kJ/mol) (Ans. -286 kJ)
5. An ideal gas of 0.1 mol was heated at 1 atm from 300 to 400 K, during a single step expansion at 1 atm. What is the q supplied, approximately? (Ans. 1330 J)
6. The internal energy of an ideal gas of 0.1 mol of 10 L is increased by 1000 J by heating at constant volume. What is the q and work done during the process? (Ans. 1000 J, 0 J)
7. An ideal gas of 0.05 mol was heated to expand under an external pressure of 1 atm from 1.2 L to 3 L at room temperature and then, compressed back to the initial volume by applying a pressure of 5 atm. Calculate ΔU, q and w for the cycle. (Ans. 66.68 kJ, 65.95 kJ, 0.730 kJ)
8. Design an experiment to test the first law of thermodynamics.
9. Make a table of work done under a variety of conditions discussed in this chapter. What does it teach?
10. If energy is conserved and mass is also conserved, how would you explain the thermonuclear reactions at a nuclear power plant or the fusion reactions of our sun or power production from a coal-fired thermal power station?

Chapter 11. Concept of Enthalpy

After completing this chapter, you will be able to:

- Recognize enthalpy as a new state function.
- Identify the properties of enthalpy and the heat capacity at constant pressure.
- Recognize Joule-Thomson expansion into vacuum and isenthalpic processes.

Goals

- Evaluate the properties of internal energy under constant pressure conditions.
- Synthesize equations relating enthalpy with temperature and pressure.
- Formulate an equation for the heat capacity under constant pressure conditions.
- Relate C_p and C_v.

11.1 Why Study This?

Enthalpy is an important thermodynamic parameter that is useful to analyze our system and processes. All processes under constant pressure conditions involve enthalpy and holding pressure constant during an experiment at atmospheric pressure is much more convenient than holding volume constant. Therefore, our immediate concern will be enthalpy rather than energy. Enthalpy is also relevant to most of the processes occurring in our daily lives, and hence, enthalpy is of interest. For example, when we burn wood in our wood stove or the fireplace, the associated energy changes are under constant pressure conditions, enthalpy changes. Holding volume constant, for example, will increase the pressure with an increase in temperature, and we will need to reinforce our stove walls to hold increasing pressure to prevent bursting of the system vessel. Thus, measurements under constant pressure conditions are more facile. However, when the pressure is kept constant there could be changes in the volume and hence, there is potential for the pressure-volume work to be performed. Thus, changes in energy of the system under constant pressure conditions would need to consider the pV work, and this leads us to heat capacity under constant pressure conditions, another important thermodynamic property to discover.

11.2 Enthalpy (H)

In the previous chapter, we examined internal energy, but its cousin is enthalpy. While investigating internal energy at constant pressure, we will discover some cool aspects of internal energy which will lead us to enthalpy. In general, laboratory measurements are often centered on enthalpy rather than energy measurements for practical reasons, described above. We will investigate the need to introduce enthalpy, its properties, and how the change in enthalpy is measured for chemical reactions or physical processes. But first, we will continue our investigation of internal energy under constant pressure conditions or for isobaric processes.

11.2.1 U as a Function of V, Isobaric Process

Previously, we have looked at the change in the internal energy under either constant temperature or constant volume conditions. These two conditions have already been discussed in the previous chapter, and so we ask, what if we keep the pressure constant, and more specifically, we ask what will be the change in the internal energy of the gas (ΔU), when the pressure is kept constant but vary the volume and temperature, for example? Keeping the pressure constant could allow for the pV work to be performed.

Consider that the system travels from the initial state (U_1, p, V_1, T_1) to a final state (U_2, p, V_2, T_2), and the change in energy, at constant pressure p is given by the following equation.

$$U_2 - U_1 = \Delta U$$

We use the first law of thermodynamics to write change in the internal energy in terms of heat supplied under constant pressure conditions (q_p) and the pV work produced against the opposing pressure (p_{opp}), as following.

$$\Delta \mathrm{U} = q_p + W = q_p - p_{opp}\,(V_2 - V_1)$$

We use the subscript p in q_p to indicate that the pressure is constant and recognize that the opposing pressure (p_{opp}) could be equal to the gas pressure because to achieve constant pressure, the opposing pressure and the gas pressure must be the same.

$$\Delta \mathrm{U} = q_p - p\,(V_2 - V_1)$$

For example, imagine that the gas is expanding against atmospheric pressure, and a facile way to do this is to allow the gas pressure to be equal to the atmospheric pressure, in the initial state (Figure 11.1). If they are not, then the gas will expand or compress till the pressures are equal, therefore, under constant pressure conditions, the gas pressure and the external pressure are to be the same. Because the initial pressure and the final pressures are the same, under constant pressure conditions, it is convenient to keep them the same as the external pressure.

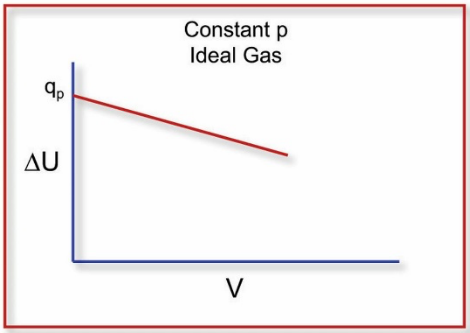

Figure 11.1 The change in U of a gas sample enclosed in a cylinder, with respect to change in volume, at constant pressure.

Under constant pressure conditions, we write the following equations where we declare initial (p_1) and final pressures (p_2), for convenience, which are the same and equal to the opposing pressure (p).

$$\Delta \mathrm{U} = q_p - (p_2\,V_2 - \,p_1\,V_1)$$

$$(U_2 + \,p_2\,V_2) - (U_1 + \,p_1 V_1) = q_p$$

Then, we group all items of the final state, then group all terms of the initial state, leaving q_p on the right. We recognize that the left side of the equation is the difference between two terms, and each term is characteristic of the state properties of the system but nothing else. The first term, for example, contains only the properties of the final state, and the second term contains only that of the initial state. Thus, each of these terms should only depend on the state of the system. Therefore, we write the equation more succinctly by substituting $H_1 = (U_1 + p_1V_1)$, and $H_2 = (U_2 + p_2V_2)$, and write the following equations.

$$H_2 - H_1 = \Delta H = q_p$$

$$\mathrm{H} \equiv \mathrm{U} + \mathrm{pV}$$

We discovered a new state function called enthalpy (H), and H must be a state function because it is the algebraic sum of U and pV. To establish that a given function is a state function, we normally construct a cyclic process and attempt to show that it does not change at the end of the cycle. However, we use alternative proof here. For example, when we define H equals U + pV, U is a state function, p and V are also state functions. So, the product of two state functions (pV) is a state function, and the sum of two state functions is also a state function. Thus, this is a nice way to deduce without constructing a cyclic process that H, which we call enthalpy, is a state function. We discovered a new state function by rearranging the terms under constant pressure conditions, but this is valid, regardless of how it was derived because it is a state function. We simplified the expression by making the substitution H = U + pV.

Since H is a state function, ΔH is a state function, and therefore, q_p is also a state function. We conclude then, the heat absorbed or released under constant pressure conditions is also a state function, and this relation is critical for all calorimetric measurements under ambient conditions. We write associated relations with changes in U, p, and V, as follows.

$$\Delta \mathrm{H} = \Delta \mathrm{U} + \Delta(\mathrm{pV})$$

Example 11.1

Describe the enthalpy changes taking place while we make a cup of coffee in the morning. Use your imagination to choose the system and the processes, appropriately. Build on the example discussed in the previous chapter.

We define the system as before, as the coffee cup with liquid water filled two-thirds the way with the boundary of the liquid separating the surroundings from the system. We heat the coffee in the microwave and transfer some energy from the surroundings into the system. The electrical energy from the utilities company is used to produce microwaves, some of which are absorbed by the water, and the water temperature rises. We are heating the system at constant pressure and hence, the temperature rise depends on the C_p values of the cup, the water, and its various other contents, if any. The magnetron which generates the microwaves is also heated during this process and those enthalpy changes are not directly related to our discussion because of the way we chose the system. If we choose the entire microwave as the system, the description will change. We also consider that some water molecules would leave the system and enter the surroundings, thus further contributing to enthalpy changes involved in the evaporation process as well. Finally, the addition of milk or sugar or both will contribute to the enthalpy changes. For example, the dissolution of sugar in the hot water involves heat of dissolution. Similarly, the dissolution of soluble contents of the coffee powder would also contribute to the heat of the solution. The addition of milk to the coffee would contribute to the enthalpy of mixing of milk with water or dissolution, or dilution, as the case may be, and might also involve the heats of solutions of some of the substances. If we now choose to stir with a spoon, then some amount of mechanical work would also be converted to heat and change the enthalpy of our system. Some amount of heat will be transferred to heat the spoon, and when withdrawn from the cup in preparation to drink, some of this enthalpy is transferred to the surroundings. Thus, we could dwell more and more on the details of our morning activity and recognize various enthalpy changes contributing to our process of coffee making.

11.2.2 H as a function of U, p, and V

Next, we investigate how enthalpy varies with other attributes of the system such as internal energy, pressure, and volume, for example. We begin with the definition of H and then write the differential expression from it, as follows.

$$\mathrm{H} \equiv \mathrm{U} + \mathrm{pV}$$

$$\mathrm{dH} = \mathrm{dU} + \mathrm{d}(\mathrm{pV})$$

Since pV is a product of two functions, we get two terms when we write the differential. Therefore, the infinitesimal change in enthalpy is by the sum of the infinitesimal changes in internal energy, infinitesimal change in the pV energy. The pV energy is equal to nRT, for an ideal gas. T is a manifestation of the kinetic energy of the system, n is kept constant here, and R is a constant. Therefore, the units of pressure and volume relate to the energy, so enthalpy is that property which is the sum of the internal energy of the system and the pV energy of the system. While internal energy is the sum of the intrinsic kinetic and potential energies of the system or the microscopic kinetic and potential energies, enthalpy is the sum of the internal energy and the energy required to create certain space for the system to occupy (Figure 11.2). Thus, there is an important distinction between internal energy and enthalpy. The very existence of the gas has a certain volume and certain pressure. Existence energy plus internal energy put together equals the enthalpy. We could have defined enthalpy this way, many textbooks do this, but the route we took provided a clearer insight into the nature of enthalpy and how it differs from internal energy, a valuable asset. For a finite change, we write the following relations, from the above discussions.

$$\Delta \mathrm{H} = \Delta \mathrm{U} + \Delta(\mathrm{pV})$$

$$\Delta H = \Delta U + \Delta(nRT) = \Delta U + \Delta n\,(RT)$$

When T is constant and the mole numbers are changing, we write Δn, shown above.

Example 11.2

For the combustion of hydrogen in pure oxygen in a constant volume calorimeter at 300 K, the heat produced was 286 kJ/mol. What are ΔU, ΔH and Δn?

The reaction converts two moles of hydrogen and one mole of oxygen into two moles of water vapor. Then, the change in mole numbers is 2-2-1= -1. The heat produced in the constant calorimeter is ΔU and is -286 kJ/mol. The change in enthalpy of this reaction is

$\Delta H = \Delta U + \Delta n\,RT = -286 + (-1 \text{ mol})(0.00831 \text{ kJ/K mol})(300 \text{ K}) = -288.5 \text{ kJ/mol}$

The answer seems reasonable because the enthalpy change is lower than the change in the internal energy as the total mole numbers of the gas decrease as the reaction progresses.

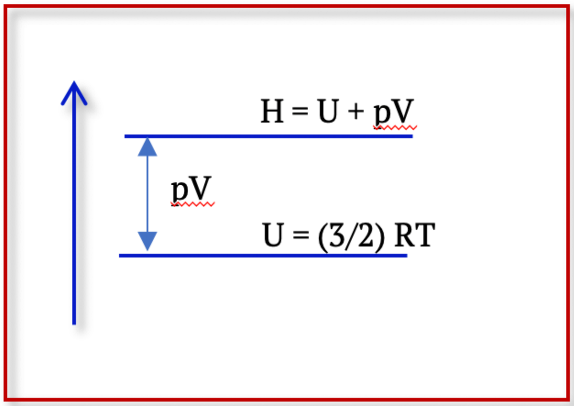

Figure 11.2 The distinction between U and H. The former is the microscopic kinetic + potential energies of the particles, in the absence of an applied field. The latter is the sum of the internal energy and the pV energy of the gas possessed by occupying a finite volume at a finite pressure.

11.2.3 H as a function of p and T

We will investigate how enthalpy depends on pressure and volume, at constant temperature and mass. Imagine that we have a gas sample in a cylinder, and we are changing both the pressure and the temperature of the system, under constant volume conditions. We can accomplish this change in a two-step process, where we change the temperature in the first step while keeping the pressure and volume constant (Figure 11.3). In the second step, we allow the pressure to vary, while keeping the temperature and volume constant. Then, we arrive at the final state with increases in both the pressure and the temperature, but volume remains constant. We can carry out this process in several different ways but thermodynamically the change in enthalpy will be the same for such processes because H is a state function. Since H is a state function, we can write the differential of H in terms of these variables.

$$\mathrm{dH} = \mathrm{dU} + \mathrm{pdV} + \mathrm{Vdp}$$

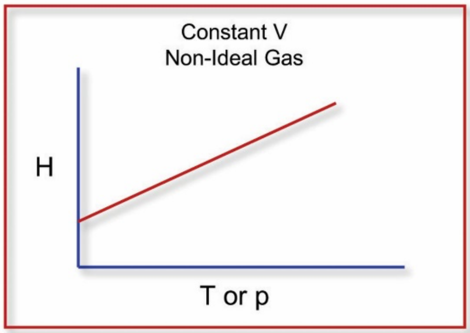

Figure 11.3 The change in H of a gas sample enclosed in a cylinder with respect to a change in temperature or pressure, under constant volume conditions.

For discussing the properties of H, we pick p and T, for convenience, which is analogous to picking V and T for discussing the properties of U. We will choose the variables p, T for H, and V, T for U, for the remainder of this book. The change in enthalpy (dH) is given by the exact differential shown below, and equal to the sum of two terms, the first one is due to contributions from the temperature, and the second term entirely due to change in the pressure. As before, the contribution from the temperature is given by the product of the rate of change of H with respect to T at constant pressure and due to the change in temperature (dT). Recall the analogy we discussed before, in terms of calculating the distance traveled by a car over a certain time at constant velocity as being equal to the rate of change of distance with time (velocity) multiplied by the time interval.

$$\mathrm{dH} = \left(\frac{\partial H}{\partial T}\right)_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp$$

Similarly, the second term in the above equation gives the contributions of pressure to enthalpy as being equal to the rate of change of enthalpy with respect to pressure at constant temperature multiplied by the change in pressure (dp). Therefore, the summation of these two terms should give the total change in enthalpy due to changes in temperature and pressure, combined. Thus, we can write any number of variables and estimate their net contribution to enthalpy in terms of each of those variables. This leads us to split this off in terms of two separate discussions of enthalpy, as following.

11.2.4 Change in H as a function of T, at constant p (isobaric process)

We take the exact differential of H and introduce constant pressure conditions and write dp = 0, and the exact differential has only the very first term, the rate of change in enthalpy with respect to temperature multiplied by the change in the temperature (dT). The second term goes to zero because dp = 0. That is, the gas is being heated from the initial temperature to the final temperature while holding pressure and volume constant (Figure 11.4), and it is analogous to the first step shown in Figure 11.3.

$$\mathrm{dH} = \left(\frac{\partial H}{\partial T}\right)_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp$$

$$\mathrm{dH} = \left(\frac{\partial H}{\partial T}\right)_p dT + 0, \qquad \text{constant p}$$

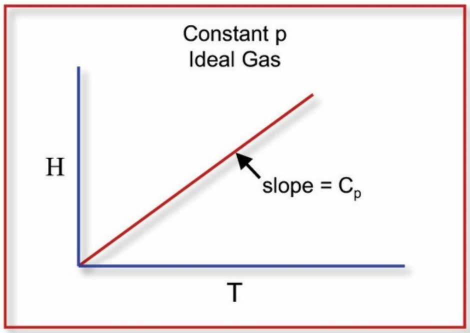

Figure 11.4 The change in H of a gas sample enclosed in a cylinder, with respect to a change in temperature under constant pressure conditions.

Our immediate task is to find the change in enthalpy (ΔH) for the above step. So, we proceed to replace the first derivative of H with respect to temperature at constant pressure with C_p, the heat capacity under constant pressure conditions. This is analogous to the heat capacity under constant volume conditions, which was defined as the rate of change of U with respect to temperature at constant volume. We can integrate the expression for dH if C_p is constant. If not, we simply express C_p in as a function of T, as we discussed in the case of U previously, and integrate the expression.

$$\mathrm{dH} = \left(\frac{\partial H}{\partial T}\right)_p dT = C_p\, dT$$

$$\int_1^2 dH = \int_1^2 C_p\, dT = C_p \int_1^2 dT$$

$$\Delta\mathrm{H} = C_p\, (T_2 - T_1)$$

We use the limits for the integral, the initial state (1) to the final state (2), assuming that C_p is constant, and we recognize that the change in enthalpy of the system (ΔH) is simply the product of the heat capacity under constant pressure conditions (C_p) and the temperature change (T_2-T_1), for all substances (Figure 11.5). If C_p varies with temperature, then we write the corresponding function of C_p with T, and integrate the whole function of H, between the initial and final states.

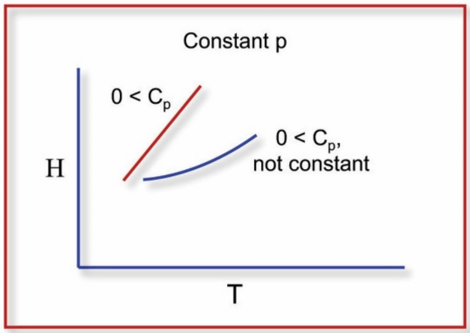

Figure 11.5 Plot of H as a function of T for an isobaric process (C_p > 0, constant, red line, > 0 but not constant, blue curve).

A plot of H vs T for an isobaric process is shown in Figure 11.5 and we have three situations: (1) C_p >0 and constant, as in the case of an ideal gas (red line, constant slope); (2) C_p is not constant but >0 (non-ideal substance, blue curve, curve with changing slope). The curvature of this must be positive or else $C_p < 0$, which is not possible, and also that $C_p \neq 0$ for any substance. We will discuss these latter aspects when we discuss entropy.

Example 11.3

Calculate the heat capacity of a gas as it is heated in a microwave oven by supplying 100 kcal of heat, under constant pressure conditions from 25 to 35 ˚C. Assume that all the supplied heat is used to heat the gas.

$C_p = \Delta H / (T_2-T_1)$ = (100 kcal)/(35-25) ˚C = 10 kcal/˚C

We will also examine a plot of C_p as a function of T. If C_p is constant, then the plot will be a line parallel to the T-axis, but if C_p is not a constant (>0) then we have a curve (Figure 11.6). The curvature can be upward or downward, that is C_p may increase or decrease with temperature for a substance. However, integration of this function between the initial and final limits gives the area under the curve and it is equal to the magnitude of ΔH, discussed above. That means, the C_p plot is a line parallel to the T-axis for the ideal gas, and any curvature is indicative of deviations from the ideal behavior. We can approximate C_p to be constant for any substance, if T_1 and T_2 are very close to each other, then we can consider that the function is linear over this small interval. Thus, we can obtain C_p and from it the value of ΔH for an isobaric process over that small temperature interval.

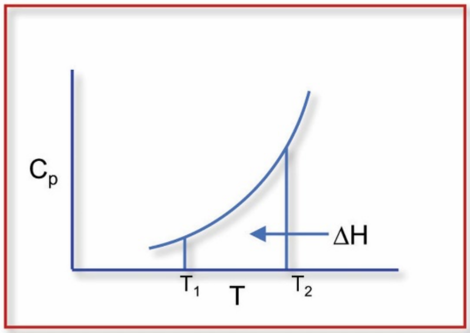

Figure 11.6 Plots of C_p vs T for an ideal gas and a non-ideal substance. C_p is constant for an ideal gas, gives a line plot with no slope, while this is a curve for a non-ideal substance. $C_p \neq 0$ nor < 0 for any substance.

Example 11.4

Calculate ΔH when 1 mole of a gas is allowed to expand isothermally from an initial volume of 5 liters to a final volume of 15 liters, against a constant external pressure of 1 atm. Assume C_p of 1 kJ/mol. Assuming ideal gas behavior, because none was mentioned, we get the following:

ΔH = C_p (T_{final} – $T_{initial}$) =Cp [p(V_2 - V_1) / nR] = 1000 $\frac{J}{mol}$ $1\ atm$ (5-15) $\frac{L\ mol\ K}{1\ mol*8.341\ J}$ = 1.47 kJ/mol

The answer has the correct sign, as the sample is being heated, and it has the correct units for enthalpy.

11.2.5 Change in H as a function of p at a constant temperature

In continuation of our discussion on the properties of enthalpy, we examine it as a function of pressure, during an isothermal process (at constant temperature). We begin with a gas sample at the initial state, hold the temperature constant, and allow the pressure to change and ask, what is the contribution of pressure to the enthalpy of the system as it reaches the final state? We begin with the exact differential of H as a function of pressure and temperature and set dT = 0 as shown below and obtain dH as a function of the rate of change of enthalpy with pressure, multiplied by the change in pressure (dp).

$$\mathrm{dH} = \left(\frac{\partial H}{\partial T}\right)_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp$$

$$\mathrm{dH} = 0 + \left(\frac{\partial H}{\partial p}\right)_T dp, \mathrm{constant\ T}$$

Thus, a plot of H vs p, at constant temperature will have a slope equal to the partial derivative of enthalpy with respect to pressure but we can't measure enthalpy directly, we can only measure the change in enthalpy (discussed later). This approach is similar to the one we used with the partial derivative of U with respect to volume, at a constant temperature, under the Joule's expansion or the free expansion.

$$\mathrm{dH} = \left(\frac{\partial H}{\partial p}\right)_T dp$$

Analogous to Joule's expansion, we can measure the rate of change of enthalpy with respect to pressure by an expansion experiment, as described later.

We can show that the change in enthalpy of an ideal gas with pressure is zero and that for liquids and solids it is close to their volume. We begin with the definition of enthalpy and write the complete differentials, as following.

$$\mathrm{H = U + pV}$$

$$\mathrm{dH = dU + pdV + Vdp}$$

Now we substitute the exact differentials for dH and dU in the above equation to obtain the following.

$$\left(\frac{\partial H}{\partial T}\right)_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV + p\,dV + V\,dp$$

$$\left(\frac{\partial H}{\partial p}\right)_T dp = \left(\frac{\partial U}{\partial T}\right)_V dT - \left(\frac{\partial H}{\partial T}\right)_p dT + \left(\frac{\partial U}{\partial V}\right)_T dV + p\,dV + V\,dp$$

Under constant temperature conditions (dT = 0), this reduces to the following.

$$\left(\frac{\partial H}{\partial p}\right)_T dp = 0 - \ 0 + \left(\frac{\partial U}{\partial V}\right)_T dV + p\,dV + V\,dp$$

Recognizing that we need the right side to be only the rate of change of enthalpy with pressure, under constant temperature conditions, we write the following.

$$\left(\frac{\partial H}{\partial p}\right)_T dp = \left(\frac{\partial U}{\partial V}\right)_T dV + p\,dV + V\,dp$$

$$\left(\frac{\partial H}{\partial p}\right)_T dp = \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right] dV + V\,dp$$

Rearranging dp at constant T, we get the following.

$$\left(\frac{\partial H}{\partial p}\right)_T = \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\left(\frac{\partial V}{\partial p}\right)_T + V$$

Since liquids and solids can only be compressed to a small extent, we can ignore the rate of change of volume with respect to pressure at constant T and write the following approximate equation.

$$\left(\frac{\partial H}{\partial p}\right)_T \approx V$$

Thus, for condensed phases, the change in enthalpy with pressure is quite small, because the molar volumes of these substances are very small when compared to those of the gases. But for gases, the above approximation of low compressibility is not valid, and the full equation becomes effective. However, the ideal gas is a special case, and we can quickly show that the enthalpy of an ideal gas is only a function of temperature and hence, under constant temperature conditions we can write the following relation.

$$H = U + pV$$

$$\left(\frac{\partial H}{\partial p}\right)_T = \left(\frac{\partial U}{\partial p}\right)_T + \left(\frac{\partial nRT}{\partial p}\right)_T = 0 + 0 = 0$$

Thus, for an ideal gas, enthalpy is independent of pressure and the Joule-Thomson coefficient is zero. For real gases, this is not the case, and the following discussion will support this assertion. These items are summarized in Figure 11.7.

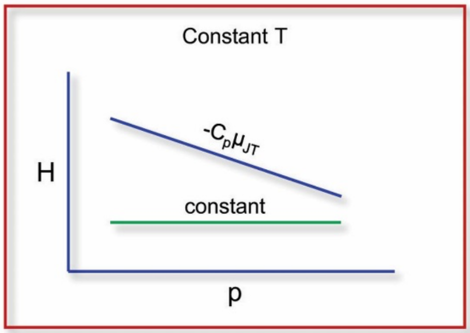

Figure 11.7 Plot of H vs p, at constant temperature for condensed phases (slanted blue line) and an ideal gas (level green line).

11.3 Isenthalpic processes

Our goal here is to obtain a relation between enthalpy, pressure, and temperature. This would enable us to construct an experiment to measure the rate of change of enthalpy with pressure. We start with the exact differential of dH, substitute C_p, set dH = 0 for the isenthalpic process, and write the enthalpy dependence on pressure, as follows.

$$\mathrm{dH} = \left(\frac{\partial H}{\partial T}\right)_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp$$

$$\mathrm{dH} = 0 = \mathrm{C}_p\,\mathrm{dT} + \left(\frac{\partial H}{\partial p}\right)_T dp$$

We rearrange the terms and express the rate of change of enthalpy with pressure at constant temperature in terms of the rate of change of temperature of the gas with respect to pressure, at constant H. The latter is the Joule-Thomson coefficient (μ_{JT}).

$$\left(\frac{\partial H}{\partial p}\right)_T = -\,\mathrm{C}_p\left(\frac{\partial T}{\partial p}\right)_H$$

$$\left(\frac{\partial H}{\partial p}\right)_T = -\,C_p\,\mu_{JT} \quad \text{where } \mu_{JT} = \left(\frac{\partial T}{\partial p}\right)_H$$

The above expression shows that the rate of change of enthalpy with pressure has a negative sign, that is enthalpy increases with a decrease in pressure. We can calculate the change in enthalpy with pressure at constant T by experimentally measuring this coefficient by the Joule-Thomson expansion experiment.

11.3.1 Joule-Thomson expansion

Imagine that the gas sample expands through a porous plug, under constant enthalpy conditions with a corresponding drop in its pressure. We carry out the process under adiabatic conditions by insulating the reactor. Thus, heat can neither enter nor leave the reactor (Figure 11.8).

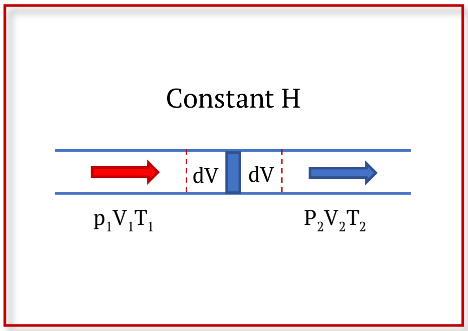

Figure 11.8 The general apparatus used to measure the Joule-Thomson coefficient, under isenthalpic conditions. The initial and final states are as indicated, and we measure the temperature and pressure differences between the right and left sides of the porous plug.

We will first show that the expansion under the above conditions, is isenthalpic and then measure the differences in the pressure as well as the temperature between the initial and final states. From these data, we can estimate the Joule-Thomson coefficient and from it, the rate of change of enthalpy with pressure is obtained.

Let the initial pressure be p_1, volume be V_1 and temperature be T_1, and the final pressure be p_2, volume V_2, and temperature T_2. Consider a small volume element dV of the gas located well before and well after the porous plug and allow the gas to expand from the high-pressure initial state through the plug into the low-pressure final state (left to right, adiabatic conditions). The gas flows under the pressure gradient, spontaneously, and in the process, work is being done by the gas on either side of the plug.

We will calculate the work done by the gas as it flows in the high-pressure region before the plug (W_{left}) and the work done as it flows after it passes through the porous plug (W_{right}) in the low-pressure region. On the left, volume changes from V_1 to 0 as all the gas in this volume exits through the plug, and we get the following. The gas performs work as it pushes the gas in front of it. We use the expression for the pdV term and integrate it over the corresponding limits.

$$W_{left} = -\int_{V_1}^{0} p_1\, dV = p_1\, V_1$$

On the right side of the plug, the volume increases from 0 to V_2 as the gas that exited the plug occupies this space. The corresponding work is given below.

$$W_{right} = -\int_{0}^{V_2} p_2\, dV = -\,p_2\, V_2$$

The total amount of work done when the gas passes through the plug is the sum of the two terms.

$$W_{total} = W_{left} + W_{right} = -\,p_2\, V_2 + p_1\, V_1$$

We write from the first law, the sum of heat and work terms and impose the restriction of the adiabatic process. After the following steps, we recognize that the process is isenthalpic.

$$\Delta U = q + W_{total}$$

$$U_2 - U_1 = 0 - p_2 V_2 + p_1 V_1$$

$$0 = U_2 - U_1 + p_2 V_2 - p_1 V_1$$

$$0 = (U_2 + p_2 V_2) - (U_1 + p_1 V_1) = H_2 - H_1$$

$$0 = \Delta H$$

We measure the pressure and temperature on each side of the porous plug, for this isenthalpic expansion, and then calculate the change in temperature divided by the change in pressure to evaluate μ_{JT}. From this value, we can obtain the dependence of enthalpy on pressure from the relation we already obtained in the previous sub-section.

$$\mu_{JT} \sim \left(\frac{\Delta T}{\Delta p}\right)_H$$

The Joule-Thomson coefficient is zero for the ideal gas, and it is positive for most gases at room temperature and below, C_p is positive for all substances. Therefore, as a gas expands under isenthalpic conditions, pressure decreases, the temperature decreases, and the gas cools! This is a fundamental principle behind refrigeration which is a very important practical application in our society.

This decrease in the temperature on expansion of gases is due to an increase in enthalpy with a decrease in pressure (Figure 11.9, green line). Note that for an ideal gas we showed that the rate of change of enthalpy with respect to pressure is zero. Hence, a comparison of the plots of H vs p is interesting, as shown in Figure 11.9. All gases have a temperature where the sign of this coefficient changes, and this is the inversion temperature.

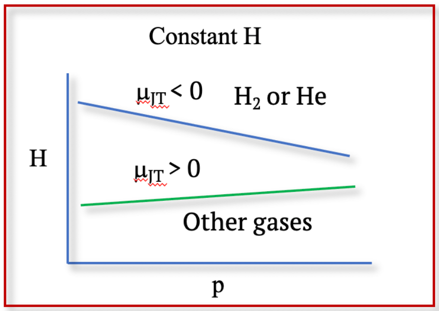

Figure 11.9 Plot of H vs p for hydrogen or helium with $\mu_{JT} < 0$ and all other gases ($\mu_{JT} > 0$) at room temperature.

Example 11.5

The sign of the Joule-Thomson coefficient depends on temperature. This is fundamentally because of the intermolecular interactions are temperature dependent. At low enough temperatures, attractive interactions dominate, as we discussed under the van der Waals equation. Then, gas expansion must overcome these forces, and internal energy of the gas is used to do the work. Thus, the gas cools.

At high enough temperatures, the repulsive interactions are dominant, and gas expansion releases energy as this repulsion is alleviated and the gas warms up. Thus, all real gases have a temperature where the sign of the coefficient changes and this temperature is called the inversion temperature.

The Joule-Thomson coefficient is negative at room temperature for hydrogen and helium, and Joule-Thomson expansion warms these gases. That is, when the gases are allowed to expand at constant enthalpy (adiabatic) conditions, then they become warmer. Other gases cool on expansion, and this is an important application in the industrial production of liquified gases.

11.4 Relation between Cp and Cv

Previously, we have examined the heat capacities under constant volume and pressure conditions, and now we will find a relationship between them, which is very useful for some key derivations later. We start with the first law of thermodynamics, and it is a very good starting point for many of the thermodynamic derivations. Then, we impose constant pressure conditions ($p_{opp} = p$), and we assume that only pV work is involved. Then we get the following equations.

$$\mathrm{dq} = \mathrm{dU} - dw$$

$$\mathrm{dq} = \mathrm{dU} + p_{opp}\, dV \mathrm{d}q_p = C_V\, dT + \left(\frac{\partial U}{\partial V}\right)_T dV + p\, dV, constant\ p$$

Because we have constant pressure conditions, the opposing pressure can be replaced with gas pressure and replace q with q_p, which is the same as H. Next, we rearrange dT terms so that we isolate C_v and C_p terms, as follows.

$$\left(\frac{\partial q_p}{\partial T}\right)_p = C_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p$$

$$C_p = C_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\left(\frac{\partial V}{\partial T}\right)_p$$

Now, we can apply the ideal gas condition and set the first term in the parenthesis to zero. We use the ideal gas law and replace the first derivative of volume with respect to temperature at constant pressure as nR/p to get the following.

$$C_p - C_V = (0 + p)\,\frac{nR}{p} = n\,R$$

$$\bar{C}_p - \bar{C}_V = R, \text{ideal gas}$$

Note that we divide both the numerator and the denominator with n to get molar heat capacities, which are indicated by a bar over the corresponding symbols. This is our standard notation to identify molar quantities. The difference in the two molar heat capacities is equivalent to the gas constant, which is a very cool result. This result is simply because the additional enthalpy stored in the system during heating under constant pressure conditions is the work done due to the expansion by the system. For an ideal gas, this is the first derivative of work Δ(pV) with respect to temperature, d(nRΔT)/dT, which is nR.

11.5 Adiabatic Expansion

An adiabatic system is insulated from the surroundings, so that heat can neither enter nor leave the system. Therefore, q = 0. Under these conditions, the first law tells us that work done during the adiabatic process is equal to the change in the internal energy of the system, which is given by the change in temperature and the heat capacity of the system, C_v. The corresponding equations are given below.

$$\mathrm{dU} = \mathrm{dq} + \mathrm{dW}$$

$$\mathrm{dU} = 0 + \mathrm{dW}$$

$$\mathrm{dU} = C_V\, dT$$

$$\Delta\mathrm{U} = \mathrm{W}_{adiabatic} = C_V\,(T_2 - T_1)$$

In the above, we assumed that C_v is constant for the integration purposes and used the initial (1) and final states (2). If C_v is not independent of temperature as in the case of a real gas, we can write it in terms of a function of temperature and complete the integration. Nevertheless, work in an adiabatic expansion is accomplished at the expense of internal energy. In the adiabatic expansion process, the masses are raised in the surroundings and hence, there will be a decrease in internal energy. Thus, there will be a decrease in the temperature of the gas during the expansion, and masses are lowered in the surroundings. This is consistent with the equations above.

Example 11.6

In the cylinders of a gasoline engine, the hot gases expand so rapidly that it can be considered as an adiabatic expansion. Given that the average temperature of gases in the cylinders is nearly 700 ˚C at 120 bar, that the gases are ignited when compressed to 1/6th of their initial volume (200 cc engine), and assuming Cv for the exhaust gases to be around 44 J/mol K independent of temperature, that the mole numbers do not increase significantly during the combustion, what is the work produced at an external pressure of 11 atm during the expansion of the combusted gases in the cylinder?

The initial temperature of the gases, initial and final volume are given. From these we calculate final temperature, and the work of expansion while both temperature and pressure decrease, under adiabatic conditions (q=0). The mole numbers and the final temperature is given by the ideal gas law as 0.069 mol and 390.1 K, respectively. The work of expansion under adiabatic conditions is given by

$$w = nC_V(T_2 - T_1) = = 0.069\,mol * 44\,\frac{J}{mol\,K}\,(390.1 - 700)K = -937\,J$$

Our approximations in the problem reduce the work produced but the sign of work is correct.

During an adiabatic compression, masses are lowered, and work is positive. The internal energy of the system is increased. Therefore, the temperature of the system increases as predicted by these equations. The value of the integral is shown geometrically in Figure 11.10 where C_V is assumed to be a non-linear function but can be analyzed in terms of a constant as well, depending on the gas used.

The area under the curve between the initial and final temperatures is the change in the internal energy and this magnitude is the same as the work produced in the surroundings during the adiabatic expansion of the gas.

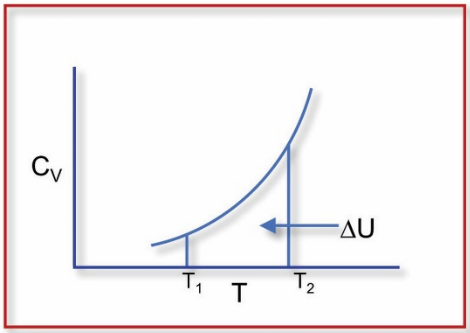

Figure 11.10 Plot of C_v as a function of temperature and the work produced in the surroundings during an adiabatic expansion (q = 0) is equal to the area under the curve (ΔU) between the two limits of temperature. C_v is constant only for an ideal gas.

When C_V is constant, the above plot will be parallel to the T-axis and the area will be a rectangle, and still, it will be equal to the work produced in the surroundings. Also, if the interval ΔT is small, then we can consider C_V to be a constant over this small interval for any gas and then integrate it.

$$\mathrm{W}_{adiabatic} = C_V\,(T_2 - T_1)$$

The above expression will be useful in discussing adiabatic processes, in the subsequent sections. Next, we will examine the adiabatic reversible expansion and recognize the differences between the reversible and irreversible adiabatic expansions. Here, we will use the relation between the two kinds of heat capacities we discovered.

11.5.1 Reversible Adiabatic Expansion

We impose an additional restriction on the above discussion, that the expansion is reversible. This immediately requires that we replace all work terms with reversible work and apply infinitesimal step expansion with equilibration after each expansion step. As usual, we begin with the first law and apply adiabatic restriction (q = 0) and reversible expansion requires that the opposing pressure be equal to p - dp, so that expansion occurs only by an interval of dV, at each step of the expansion. Thus, we have the following set of equations relating dU with dV and then use the ideal gas law to write pressure in terms of volume.

$$\mathrm{dU} = \mathrm{dq} + \mathrm{dw}$$

$$C_V\, dT/T = 0 - p\, dV = -\left(\frac{nR}{V}\right) dV$$

So far, we have used the conditions of adiabaticity, reversibility, and ideal gas behavior and now we can integrate both sides over the initial state (1) and the final state (2). The left side has only temperature terms and C_V is a constant for the ideal gas. On the right side, we have only the volume terms and hence, we can readily integrate this expression to get the relation between the temperature and volume of the system, as worked out below.

$$\int_1^2 C_V\, \frac{dT}{T} = -\mathrm{nR} \int_1^2 \frac{dV}{V}$$

$$C_V\, \ln\left(\frac{T_2}{T_1}\right) = -\mathrm{n\,R} \ln\left(\frac{V_2}{V_1}\right)$$

$$\ln\left(\frac{T_2}{T_1}\right) = \frac{nR}{C_V}\, \ln\left(\frac{V_1}{V_2}\right)$$

We absorbed the negative sign in the second step by flipping the logarithmic function in the third step and now we can further simplify this expression by taking anti-logs on both sides to obtain the following.

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{V_1}{V_2}\right)^{\left(\frac{nR}{C_V}\right)}$$

The above provides a nice relationship between the initial and final variables of the system, while pressure and n are constants. We can simplify this further. First, we write nR in terms of heat capacities that we derived earlier, and then we define gamma (γ) as the ratio of heat capacities under constant pressure and constant volume conditions.

$$\frac{nR}{C_V} = \frac{\bar{C}_p - \bar{C}_V}{\bar{C}_V} = \gamma - 1$$

Then, the relation between the temperatures and volumes of our system are as below. $\left(\frac{T_2}{T_1}\right) = \left(\frac{V_1}{V_2}\right)^{(\gamma-1)}$

$$\gamma = \frac{C_p}{C_V}$$

The above equation can be even further simplified or written in a neater form by simply cross multiplication of the terms, as follows.

$$T_1\, V_1{}^{(\gamma-1)} = T_2\, V_2{}^{(\gamma-1)}$$

For a reversible adiabatic expansion involving an ideal gas, changing from state 1 to state 2, the initial and final temperatures, as well as their volumes, are related via gamma, the ratio of heat capacities. This step further allows us to relate the initial and final pressures of the system via the ideal gas law, as following, where we replace the temperature terms with the corresponding pressure terms (T = pV/nR) and cancel common terms on both sides of the equation to get the pressure-volume relation.

$$p_1\, V_1\, V_1{}^{(\gamma-1)} = p_2\, V_2\, V_2{}^{(\gamma-1)}$$

$$p_1\, V_1{}^{\gamma} = p_2\, V_2{}^{\gamma}$$

Thus, the p, V, and T terms are related in an adiabatic reversible expansion in a particular way to satisfy the above equations.

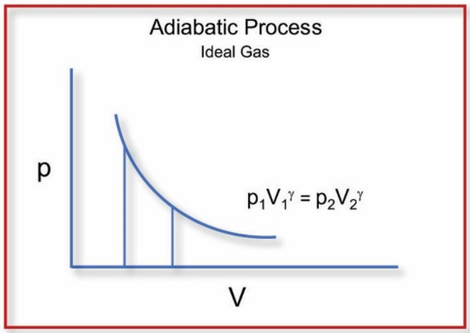

Figure 11.11 Plot of p vs V for an adiabatic reversible expansion (q = 0, p_{opp} = p), the area under the curve is the reversible work produced, and it is also the decrease in the internal energy of the system (∆U).

The pressure-volume plot for an adiabatic reversible expansion of an ideal gas is shown in Figure 11.11. The gas expands reversibly from the initial state to the final state with a decrease in temperature and therefore, this is not an isotherm and not a plot of Boyle's law. It may appear similar but the decrease in pressure is larger here because the temperature is also decreasing as the gas expands. Thus, the curve drops off more rapidly than in the case of reversible isothermal expansion.

Example 11.7

When an ideal gas of 0.2 mol expands adiabatically from 2.5 L and 10 atm to a final volume of 3.5 L, calculate the final pressure and temperature.

We will use the ideal gas law and obtain the ratio of heat capacities to be (3.5 nR/2.5 nR) and then get the initial temperature from the ideal gas law to be 507.8 K. Using the adiabatic pV relation between the initial and final states, we get the final pressure as follows. Then, we get final temperature as 443.8 K, using the ideal gas law.

$$p_1\,V_1{}^\gamma = p_2\,V_2{}^\gamma \;or\; p_2 = \frac{p_1\,V_1{}^\gamma}{V_2{}^\gamma} = \frac{10\,atm * 2.5^{1.4} * L^{1.4}}{3.5^{1.4} * L^{1.4}} = 6.24\,atm$$

In summary, we have shown that the work produced in an adiabatic expansion is equal to the change in the internal energy of the system because q = 0. Since q is zero, the work was produced in the surroundings at the expense of the internal energy, and this results in a decrease in the temperature of the system. This may appear counterintuitive that if q is zero, the temperature should not change but we must keep in mind that masses are raised in the surroundings and the internal energy is converted to useful work, and hence, the temperature of the gas decreases. Adiabatic expansion can produce cloud formation and plays an important role in liquefaction as well. With key attributes of enthalpy under our belt, so far, we are now ready to examine enthalpy changes in chemical transformations.

11.6 Molecular interpretation

While the internal energy of an ideal gas is the purely kinetic energy of the gas particles ((1/2) mc^2), enthalpy is the sum of the internal energy and the energy needed for creating certain space for the gas to occupy. This is simply because there are no interparticle interactions in an ideal gas, and all its energy is manifesting as the kinetic energy, the internal energy of the gas. But enthalpy is the sum of the internal energy to create the substance and the energy for creating the volume needed for the gas to occupy at a certain pressure. Real gases, on the other hand, do have kinetic energy as the ideal gas but also have interparticle interactions as well as intra-particle interactions (excluding mono atomics), and hence, they do have potential energy. The enthalpy is the sum of these plus the pressure-volume energy. While internal energy is viewed as the energy to create the substance, enthalpy is the energy needed for making the system, and also for its existence to occupy some space.

The enthalpy of a gas depends on the pressure and temperature of the system. The effect of temperature on the enthalpy of the gas is readily understood in terms of the above molecular descriptions. As we increase the temperature of the gas, the particles gain additional kinetic energy and travel at higher speeds, some of the energy is used to increase the potential energy as well as the pressure of the gas. Thus, the enthalpy of the system increases with an increase in temperature. This rate of change in enthalpy of a substance at constant pressure (C_p) is a characteristic quantity.

Heat capacity of a substance under constant pressure conditions is due to all reservoirs, where the energy is stored, but the heat supplied is also used to perform work across the boundary. Because the gas is under constant pressure, the volume increases as we increase the temperature, and work is performed against the opposing pressure using part of the q supplied. Therefore, heat capacity under constant pressure conditions is greater than the heat capacity under constant volume conditions. Thus, various types of motions, as well as the work, contribute to the heat capacity.

11.7 Applications in daily life

Enthalpy changes manifest on most day-to-day events under the guise of thermodynamics, in real life, because most of our daily transactions are carried out at atmospheric pressure. Heating a cup of coffee or keeping the house warm in winter, or cool it during the summer, all require energy transactions at constant pressure, and hence, we are influenced by enthalpy changes, daily.

11.8 Key Points

1. The enthalpy is the sum of the internal energy and the pressure-volume energy. Thus, while internal energy is the energy used to make the particle, enthalpy is this energy plus the energy needed to create space against external pressure for the system to exist. Thus, the pressure-volume energy is the key difference between the two state functions.
2. When we heat a gas sample to raise its temperature, at constant pressure, part of the heat supplied is used to raise the temperature of the gas, and part of it is used to perform work in the surroundings. As we raise the temperature under constant pressure conditions, the volume increases, and hence, work will be done in the surroundings or masses will be raised. Thus, C_p will be larger than C_v, qualitatively speaking.
3. Heat capacity under constant pressure conditions is the rate of change of enthalpy with the temperature at constant pressure and it is always positive. It can also be a function of temperature or a constant, depending on the substance under study. It is not zero or negative for any substance.
4. The enthalpy is also a function of pressure and the rate of change of enthalpy with pressure is measured indirectly by measuring the rate of change of temperature with pressure under isenthalpic conditions. This is zero only for an ideal gas but can be positive or negative for real gases.

11.9 New Terms and units

Enthalpy, heat capacity under constant pressure conditions, Joule-Thomson expansion, calorimetry, the heat of reaction, heat of formation, standard enthalpies, Hess' law, the heat of solvation, heat of dilution, heat of combustion, bond enthalpies, and bond energies. The units of enthalpy are the same as that of energy, which we have already discussed in earlier chapters. Units of heat capacity are simply energy/K or energy/˚C.

$$\Delta H = \Delta U + \Delta(pV) \qquad \Delta H = C_p\,(T_2 - T_1) \qquad W_{adiabatic} = C_V\,(T_2 - T_1)$$

$$q_p = \Delta H = (\text{specific heat} \times \text{mass})\,(T_2 - T_1) \qquad \mu_{JT} = \left(\frac{\partial T}{\partial p}\right)_H \qquad \left(\frac{\partial H}{\partial p}\right)_T = -\,C_p\,\mu_{JT} \qquad \bar{C}_p - \bar{C}_V = R$$

$$T_1\,V_1^{(\gamma-1)} = T_2\,V_2^{(\gamma-1)} \qquad p_1\,V_1^{\gamma} = p_2\,V_2^{\gamma}$$

11.10 Self reflection

1. Imagine you are traveling from your home to the university in your car. Sketch a diagram showing the total enthalpy of the system as a function distance as you travel from home and explain each segment.
2. Plot a 3D graph of H, V, and T for an ideal gas and a real gas as they expand at constant p or constant volume.
3. The molar heat capacities at constant pressure (J/mol K) of few gases are Methane (35.69), CO_2 (36.94), H_2O_{vapor} (75.33), He (20.79), and Ar (20.79). Test the hypothesis that heat capacity is proportional to the total degrees of freedom of a gas.
4. Given the space of your dorm, discover examples of heat capacities at constant pressure and constant volume.

5. When 11 g of sugar was burnt in oxygen, in a bomb calorimeter, 1000 J of heat was released. What is the change in the mass due to the chemical reaction?
6. Compare and contrast the properties of internal energy and enthalpy. What is common and what is different with each of these?

11.11 Further reading

1. https://ocw.mit.edu/courses/chemistry/5-60-thermodynamics-kinetics-spring-2008/video-lectures/lecture-4-enthalpy/
2. https://ocw.mit.edu/high-school/chemistry/exam-prep/reactions/thermodynamics/heat-of-formation/

11.12 Self Tests

1. For an ideal gas, what is the difference in molar heat capacities at constant pressure and volume?

a. nR

b. R

c. RT

d. ΔU

2. How is the change in enthalpy of the system due to a process at constant pressure expressed?

a. dq

b. -dq

c. 0

d. dU + pdV

3. What is the change in molar enthalpy of nitrogen when it is heated from 298 K to 373 K (C_p = a + bT, a = 28.5 J K^{-1}, b = 3.8×10^{-3} J K^{-2} mol^{-1})

a. 2.24 J mol^{-1}

b. 2.24 kJ mol^{-1}

c. 0

d. 224 kJ mol^{-1}

4. Which of the following is the correct expression for the ratio of heat capacities of gases at constant pressure and constant volume

a. C_v/C_p

b. C_p/C_v

c. $-C_v/C_p$

d. $2C_p/C_v$

5. For an ideal gas the Joule-Thomson coefficient is equal to ________ .

a. the pressure

b. the heat capacity

c. zero

d. need more information

6. Work done in an isothermal reversible expansion of 1 mol of a gas from 1 to 5 L, at 300 K is

a. <1 kJ

b.>1 kJ

c.0 kJ

d. not sufficient information

e. none of these

7. Work done in an adiabatic reversible expansion of 5 mol of a gas of heat capacity at constant volume of 1 kJ/K, from an initial temperature of 300 K to a final temperature of 400 K is

a. < 90 kJ

b. > 90 kJ

c. 0 kJ

d. can’t say

e. none of these

8. The change in enthalpy due to the free expansion of an ideal gas is

a. zero

b. <0

c. ±infinity

d. >0

e. none of these

9. Which of the following is the correct expression for the heat capacity under constant pressure conditions?

a. $\frac{dU_p}{dT} = C_p$

b. $\frac{dq_p}{dT} = C_p$

c. $\frac{dp_p}{dT} = C_p$

d. none of the above

10. As a real gas expands at constant enthalpy, its temperature

a. increases due to interparticle interactions

b. does not change

c. decreases due to interparticle interactions

d. decreases

e. none of the above

11. As an ideal gas expands under isobaric conditions, its enthalpy

a. increases

b. does not change

c. decreases due to interparticle interactions

d. decreases

e. can’t say

12. As a real gas expands adiabatically, its enthalpy

a. increases due to interparticle interactions

b. does not change

c. decreases due to work that appears at the surroundings

d. equals to ΔU+Δ(pV)

e. none of the above

13. The expression for the first law of thermodynamics is

a. dH = dq - dw

b. dH + dq = dw

c. dH-dq = dw

d. dH + dw = dq

e. none of the above

14. Change in ΔH for isobaric heating of an ideal gas is

a. $\Delta \mathrm{H} = C_p\ (T_2 - T_1)$

b. does not change

c. zero

d. $\Delta \mathrm{H} = C_p\ (T_1 - T_2)$

e. none of the above

15. When an ideal gas is heated isobarically, the value of $\left(\frac{\partial H}{\partial T}\right)_p dT$

a. increases

b. is zero

c. decreases

d. unchanges

e. none of the above

16. Plot of H vs V for an ideal gas at constant temperature is

a. exponential

b. linear with no slope

c. linear with negative slope

d. linear with positive slope

e. none of the above

17. For an ideal gas, the value of $\left(\frac{\partial H}{\partial p}\right)_T$

a. increases with T due to interparticle interactions

b. does not change with temperature

c. decreases with temperature due to interparticle interactions

d. decreases with increasing pressure

e. none of the above

18. For a real gas, the value of $\left(\frac{\partial H}{\partial p}\right)_T$

a. 0

b. >0 and does not change with temperature

c. <0 or >0 but not equal to zero

d. >1

e. none of the above

19. For a real gas, the value of H is approximately

a. (5/2) nRT

b. ½ nRT

c. nRT

d. 2 nRT

e. none of the above

20. For an idea gas, the value of $\left(\frac{\partial H}{\partial p}\right)_T$ is

a. (3/2) nRT

b. 3 nRT

c. RT

d. 2 nRT

e. none of the above

11.13 Self Tests Key

1. b, 2. d, 3. b, 4. b, 5. c, 6. a, 7. b, 8. a, 9. b, 10. d, 11. a, 12. d, 13. e, 14. a, 15. c, 16. b, 17. b, 18. e, 19. a, 20. e

11.14 Problems

1. An ideal gas (1 mol, 1 atm) is heated from 290 to 295 K at constant pressure. What is the heat absorbed? (Ans. 103.9 J)
2. A gas sample of 0.1 mol was heated under constant pressure of 1 atm from 300 to 600 K. What is ∆H, q and w? (Ans. 623.6 J, 623.6 J, and -249.4 J)
3. A natural gas car burns methane in oxygen and produces work in a cylinder like that of an internal combustion gasoline engine. If 1 mole of methane is completely converted in just enough pure oxygen with a catalyst into water at room temperature (300 K), what is the work produced in a one-step expansion against the atmospheric pressure? (heat of combustion of methane = 890 kJ/mol; consider the average Cp of the products as 2.5 nR) (Ans. -356 kJ)
4. An ideal gas of 2 mol was heated at 1 atm from 300 to 400 K, during expansion at constant pressure. What is the q supplied, approximately? (Ans. 4.157 kJ)
5. The enthalpy of an ideal gas of 0.5 mol of 12.3086 L at 300 K is increased by 1000 J by heating at 1 atm. What are q and w that appear during the process? (Ans. 1000 J, 400 J)
6. An ideal gas of 1 L was heated to 596.3 K to expand under constant external pressure of 1 atm to 2 L from room temperature and then, compressed back isothermally to the initial volume by applying pressure. Calculate ∆H, q and w for the cycle. (Ans. 253 J, 50.7 J, 101.3 J)
7. A gas sample of 0.1 mol was heated under constant pressure of 1 atm from room temperature to 500 K and compressed reversibly back to its initial state. What are ∆U, ∆H, q and w for the cycle? (Ans. 0 J, 0 J, 0 J, 0 J,)
8. What is the change in molar enthalpy of nitrogen when it is heated from 298 K to 373 K (C_p = a + bT, a = 28.5 J K^{-1} mol^{-1}, b = 3.8×10^{-3} J K^{-2} mol^{-1}) (Ans. 2.98 kJ mol^{-1})
9. Design an experiment to measure the temperature dependence of enthalpy of a reaction.

Chapter 12. Enthalpy and Calorimetry

After completing this chapter, you will be able to:

- Define the enthalpies of reactions, standard enthalpies, and enthalpies of formation.
- Apply Hess's law to measure enthalpy changes of chemical reactions.
- Distinguish between bond energies and bond enthalpies.

Goals

- Define enthalpies of standard states, reactions and physical processes.
- State Hess law and design methods to measure heats of reactions.
- Define bond energies and bond enthalpies
- Synthesize an equation for the temperature dependence of reaction enthalpies.

12.1 Why study this?

In addition, we will also examine the enthalpies of chemical reactions because we can make these measurements routinely using highly sensitive modern calorimeters that operate under constant pressure conditions. The bomb calorimeter operates under constant volume conditions and hence, it is loaded with heavy walls which limits its sensitivity. Constant pressure calorimeters on the other hand, much easier to work with as they have thinner walls, low heat capacities, and high sensitivities. These calorimetric measurements are useful to obtain bond energies and bond enthalpies, which are extremely valuable for chemists. Enthalpy is a key player in thermodynamic analysis of chemical reactions.

12.2 Heats of reactions

In chemistry, we are interested in studying chemical processes that are analogous to the physical processes such as expansion or compression, described above. One distinction between chemical reactions and physical processes is to be made. The total mole numbers could change during a chemical reaction where the reactants are converted to products. In a physical process, we generally keep the mole numbers constant. In both cases, we are using a closed system so that only energy can pass through the boundary of the system. It is routine to use a calorimeter to monitor the energy changes taking place during a chemical reaction. This is a device that will allow us to accurately measure the changes in the temperature of the water in the surroundings and thus, q can be estimated from these data. Modern calorimeters, however, do not measure such temperature changes but measure q directly.

12.2.1 Heat of reaction under isobaric conditions

It is convenient to carry out a chemical reaction under constant pressure conditions by leaving the calorimeter to equilibrate with the atmospheric pressure. This way, we don't need to worry about constructing a vessel that will keep the volume constant during the process of interest. Under constant volume conditions, the process could potentially increase or decrease the pressure, and thus requiring thick, strong walls for the calorimeter. Since we prefer to keep the pressure constant, we avoid this issue. Under constant pressure conditions, we examine the enthalpy changes rather than internal energy changes.

The heat of a reaction under constant pressure conditions is defined as equal to the change in enthalpy (ΔH) of the system, when the reactants at pressure p temperature T are converted to products, at the same pressure and temperature. Mathematically we write the chemical reaction in the following manner.

$$\text{Reactants} \rightarrow \text{Products} + \Delta\text{H} \qquad (\text{constnat p, T})$$

In this experiment, we carry out a chemical transformation from the initial state where we have pure reactants under a specific set of conditions of pressure and temperature, and these are completely converted to pure products under the same set of conditions of pressure and temperature. We express this value (q_p) in terms of the enthalpies of the pure reactants and pure products, under constant pressure and temperature conditions, as follows.

$$\Delta\text{H} = q_p = H_{products} - H_{reactants}$$

$$q_p = \Delta\text{H} = (\text{specific heat} \times \text{mass})\,(T_2 - T_1)$$

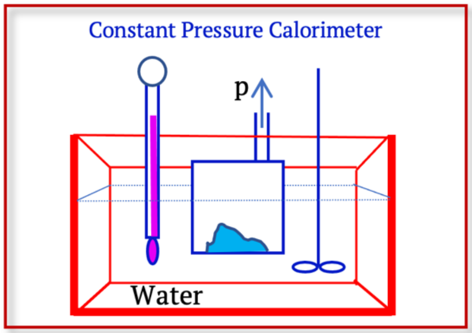

Figure 12.1 Constant pressure calorimeter (open to air) is used to measure the heats of reactions (ΔH). The mass of water around the reaction chamber is fully insulated from the surroundings to maintain adiabatic conditions. The change 0n the temperature of the water, before and after the reaction, is measured to calculate q_p.

For this purpose, we use the constant pressure calorimeter shown in Figure 12.1. At constant pressure conditions, q_p is equal to ΔH, and it is in turn given as the enthalpy of products at the final state minus enthalpy of reactants in the initial state, all kept at the same temperature and pressure. We may have more than one reactant and more than one product, then we sum all the enthalpies of all reactants from the enthalpies of all the products, at the same pressure and temperature to get the enthalpy of the reaction or the heat of reaction.

$$Fe_2O_3 \text{ (solid)} + 3H_2 \text{ (gas)} \rightarrow 2Fe \text{ (solid)} + 3H_2O \text{ (liquid)} + \Delta H$$

Take the example of iron oxide, in the solid state, reacting with hydrogen gas in the gas phase, giving rise to reduced iron in the solid form and water in the liquid state, under constant pressure and temperature conditions (shown above). We are obligated to balance the chemical equation such that the number of atoms of one kind on the left side of the chemical equation equals the same number of the same kind of atoms on the right side. This is the important reason why we spend so much time talking about how to balance a chemical equation at the introductory levels. The laws of thermodynamics require that we have the same number of atoms in the final state of the same kind, as there were in the initial state. We can't create or destroy an atom during a chemical reaction, we can only alter its oxidation state. Therefore, we have to balance the chemical equation.

For that reason. initial and final states should have the same number of hydrogens, same number of oxygens, same number of carbons, and so on. Therefore, one mole of iron oxide reacts with three moles of hydrogen gas to produce two moles of iron and three moles of liquid water. We are obligated to specify the states of each of the substances present in our reaction. So, iron oxide is in the solid form (s), hydrogen gas in the gas phase, iron in the solid state, and water is in the liquid state. So, this is the overall chemical reaction. Then, ΔH of this reaction is equal to the enthalpy of products minus reactants.

$$\Delta \mathrm{H} = q_p = (2H_{Fe,solid} + 3H_{H_20,liquid}) - (H_{Fe_2O_3,solid} + 3H_{H_2,gas})$$

The reaction is carried out the constant pressure conditions, and we measure q at the boundary by measuring the temperature of water in the calorimeter as the reaction progresses. The enthalpy is obtained from the change in the temperature of the mass of water surrounding the calorimeter, as follows.

$$q_p = \Delta \mathrm{H} = (\text{specific heat} \times \text{mass})\,(T_2 - T_1)$$

Mass of the calorimeter and its specific heat are also considered. But here, we show only that of the mass of water for simplicity, and ΔH is estimated from the initial temperature T_1, the final temperature T_2, specific heat of water and its mass. This is why science is wonderful. You're able to measure something you cannot see, and able to measure something you can feel as being warm or cold, but you can quantify it exactly.

Example 12.1

Calculate the heat released when 1 mol of monobasic acid was mixed with 1 mol of a monobasic base in a closed Styrofoam container (calorimeter) with a total mass of 1 kg of water (specific heat 4.184 J/g ˚C)?

The temperature rose from 25 ˚C to 31.5 ˚C during the titration, neglect the calorimeter mass and any heat loss.

We calculate the heat released during the acid base titration by calculating the amount of water needed to raise its temperature by 1 K, as the reaction occurs.

$$q_p = \Delta\mathrm{H} = (\text{specific heat } \times \text{ mass})\,(T_2 - T_1)$$

$$= \left(4.184\,\frac{J}{g * {}^{\circ}C} * \frac{{}^{\circ}C}{K} * 1\,kg\,\frac{1000g}{kg}\right)\left((31.5 + 273.15)K - (25 + 273.15)K\right) = 27196\,J/mol$$

12.2.2 Heats of reactions under isochoric conditions

Similarly, we could carry out the reaction in a constant volume calorimeter (Figure 12.2) where thick walls of the calorimeter and air-tight lid keep the volume constant, during the chemical reaction. For this reason, it is termed the bomb calorimeter. The q_v measured is equal to ΔU, which is the energy of the reaction, measured under constant volume and temperature conditions.

$$q_V = \Delta\mathrm{U}$$

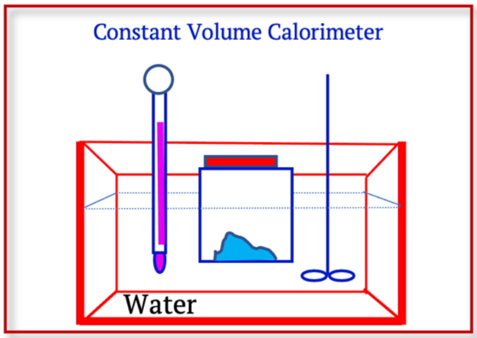

Figure 12.2 Constant volume calorimeter (closed) is used to measure ΔU, at constant volume. The mass of water around the reaction chamber is fully insulated from the surroundings to maintain adiabatic conditions. The change in the temperature of the water is measured to calculate q_v and from it ΔU for the chemical reaction.

As the reaction progresses in the calorimeter, heat may be released or absorbed and the temperature of water in equilibrium with the calorimeter could change. This temperature change is recorded, and q_v estimated, and from this, the value of the energy of reaction (ΔU) is calculated, under constant volume conditions. From ΔU, we can readily obtain ΔH, considering the change in the number of moles that have occurred due to the chemical transformation. Then, ΔH is estimated from ΔU as follows.

$$\Delta\mathrm{H} = \Delta\mathrm{U} + \Delta(\mathrm{pV})$$

$$\Delta\mathrm{H} = \Delta\mathrm{U} + \Delta(\mathrm{nRT}) = \Delta\mathrm{U} + \Delta\mathrm{n}\ \mathrm{R}$$

$$\Delta\mathrm{n} = n_{products} - n_{reactants}$$

In the above conversions, we assume that all reactants and products are ideal gases and apply the ideal gas law. When these conditions are not satisfied, we have to use the appropriate equations of state for each of the substances used to obtain the ΔpV term. For solids and liquids, this is small. We can use the van der Waals equation, for example, for van der Waals gases. Thus, calorimetric data are obtained for chemical reactions and these data are of importance to calculate bond enthalpies and bond energies.

Example 12.2

The change in the internal energy of the system when 1 mol of methane was completely burnt in pure oxygen was 890 kJ/mol.What is the change in the enthalpy during this process?

We need to estimate the change in the number of moles when methane is burnt in oxygen, and a balanced chemical equation tells us that it is (3 moles of products – 3 moles of reactants), Δn=0.

$CH_4 + 2O_2 \rightleftarrows 2H_2O + CO_2$, Hence,

$$\Delta H = \Delta U + \Delta(nRT) = \Delta U + 0\,R = 890\ \mathrm{kJ/mol}$$

The answer makes sense because the units are correct, the sign is correct, and the chemical reaction has been balanced correctly.

Three things are important in recognizing the heat of a reaction, first, that the chemical reaction may involve changes of phases of the reactants/products and hence, the heat of the reaction includes the corresponding enthalpy changes for each of the phase transitions.

Secondly, we declare the heat of reaction as a product from the chemical reaction, which it is. If the reaction is exoenthalpic then the sign of ∆H is negative, the system is losing that amount of enthalpy to the surroundings. If the reaction is endo enthalpic, then the system is gaining that amount of enthalpy during the reaction and the sign of ∆H is positive. Thus, the sign of ∆H automatically accounts for the case in point.

The third point is that we are obligated to balance the chemical equation such that the number of atoms of one kind on the left side of the equation exactly equals the number of the same kind of atoms on the right side. This is the law of conservation of mass, and it is an essential reason why we spend so much time recognizing how to balance chemical equations. This is simply because we can't create an atom or destroy an atom in a chemical reaction. For example, the reactants and products must have the same number of hydrogen atoms, the same number of oxygen atoms, the same number of carbon atoms, and the same numbers of all other elements as well. We recognize that the total mole numbers can change during a chemical reaction, but this does not violate the law of conservation of mass. Therefore, the chemical reaction must be balanced to get the values of the reaction enthalpies or reaction energies.

Example 12.3

Consider the following chemical reaction and discuss the heat of the reaction, in detail.

$$Al_2O_3\ (solid) + 3H_2(gas) \rightarrow 2Al\ (solid) + 3H_2O\ (liquid) + \Delta H$$

In the chemical reaction above, aluminum oxide in the solid state reacts with hydrogen gas from the gas phase, giving rise to reduced aluminum in the solid form plus water in the liquid state.

And therefore, in the case of the above chemical reaction, we have one mole of aluminum oxide reacting with three moles of hydrogen gas to produce two moles of aluminum and three moles of liquid water. We are obligated to specify the standard states of each of the substances present in our reaction. So, iron oxide is in the solid form, hydrogen in the gas phase, their corresponding standard states. On the product side, metallic iron in its standard state of the solid, and water is in its standard state, which is liquid. We can further specify the temperature at which the reaction is being carried out, and we expect that the reaction is carried out under constant pressure conditions of 1 atm unless specified otherwise. Then, ∆H for this chemical transformation is equal to the enthalpy of products minus reactants, in their respective standard states, as given below.

$$\Delta H = H\ (2Al, solid) + H\ (3H_2O, liquid) - H\ (Al_2O_3, solid) - H\ (3H_2, gas)$$

Thus, the sum of standard enthalpies of 2 moles of aluminum in the solid phase, that of 3 moles of water in the liquid phase is the total enthalpy of the products, and the enthalpy of reactants is the sum of enthalpies of one mole of aluminum oxide in the solid form and three moles of hydrogen gas in the gas phase. The difference in the enthalpies of the products and reactant is the reaction enthalpy, for this chemical transformation.

We recognize that the energy of reaction (∆U) can be readily obtained for this chemical reaction from its ∆H value using the previously discussed relation, ∆H = ∆U + ∆n RT. The change in the mole numbers is the difference in the total mole numbers of products and reactants. In the above example, we have 3 moles of water and 2 moles of aluminum being produced from 1 mole of aluminum oxide, and 3 moles of hydrogen. Thus, ∆n for this reaction is 5-4 = 1. Thus, we can readily obtain ∆U value if we know the temperature at which the reaction was carried out. On the other hand, if ∆n = 0, then ∆H and ∆U are the same.

12.2.3 Exothermic and endothermic reactions

Calorimeters are typically used to measure the heat released or absorbed during a reaction. When the products have less enthalpy than the reactants, then the chemical reaction releases enthalpy in the surroundings. These are termed exothermic reactions (Figure 12.3A). For example, the burning of magnesium in the air produces large amounts of heat, and so is the burning of gasoline. In general, we can say that all combustion reactions are exothermic.

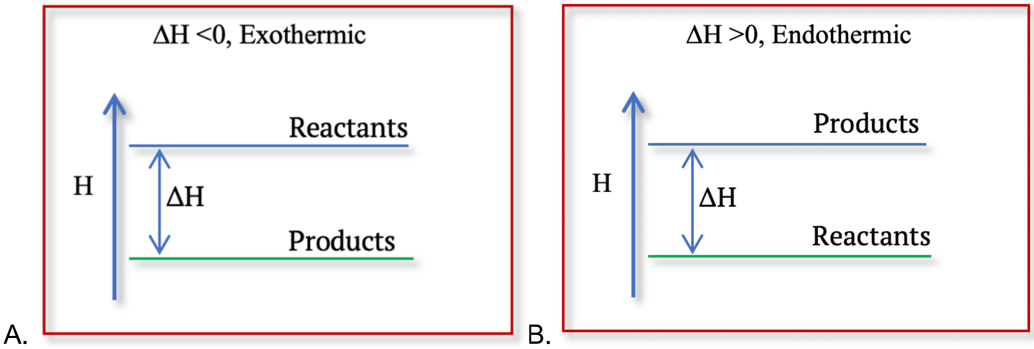

Figure 12.3 A. Exothermic reactions where product formation releases enthalpy, products have lower enthalpy than reactants, and ΔH <0, the system loses enthalpy. B. Endothermic reactions where product formation absorbs enthalpy, products have higher enthalpy than reactants and ΔH >0, the system gains enthalpy.

When the products have a higher enthalpy than the reactants, then the chemical reaction absorbs enthalpy from the surroundings and the system gains enthalpy. These are termed endothermic reactions (Figure 12.3B). For example, cracking of alkanes to form lower molecular weight products, electrolytic decomposition of sodium chloride, dissolution of ammonium chloride in water (physical process), and the most important chemical reaction on this planet, the photosynthesis where water and carbon dioxide react absorbing the sunlight. In general, there is a misconception that endothermic reactions are not spontaneous, but that is incorrect. They can happen spontaneously, as in the case of photosynthesis or dissolution of ammonium chloride or melting of ice to water, or evaporation of water to its vapor.

12.2.4 Temperature dependence of the heat of a reaction

Since we learned that enthalpy is a function of temperature, we do expect the heat of reaction will also be a function of temperature. This is important, because if we know the temperature dependence of the heat of reaction and the heat of reaction at one temperature, then we could calculate the heat of reaction at another temperature, without having to measure at that temperature. For example, we may have carried out a reaction at room temperature and measured ΔH, but then we may need the value of ΔH at some other temperature. Do we have to repeat the experiment at this other temperature? It will be convenient If we don't have to repeat the experiment and be able to calculate it from other properties of the system. And that's the purpose of this discussion. We start with the definition of the $\Delta H_{reaction}$ as the difference in the enthalpies of the products and reactants, and then we differentiate the equation with respect to temperature on both sides.

$$\Delta H_{reaction} = H_{products} - H_{reactants}$$

$$\frac{d\Delta H_{reaction}}{dT} = \frac{dH_{products}}{dT} - \frac{dH_{reactants}}{dT}$$

$$\frac{d\Delta H_{reaction}}{dT} = C_{p,products} - C_{p,reactants} = \Delta C_p$$

For all practical purposes, we will keep the pressure constant for convenience, the differential of the heat of reaction with the temperature at constant temperature is the difference in the first derivatives of the enthalpies of the products and reactants. Then, we recognize that these first derivatives are essentially the heat capacities at constant pressure (C_p). Thus, we express the first derivative of the heat of reaction as the difference in the heat capacities of the products and reactants, under constant pressure (ΔC_p). Now, we can integrate this expression and obtain reaction enthalpy as a function of temperature, our immediate goal, as following. Let the initial and final limits of the temperatures of interest be T_1 and T_2, and we integrate the above expression between these limits.

$$\int_1^2 d\Delta H_{reaction} = \int_1^2 \Delta C_p \, dT$$

$$\Delta H_{2,reaction} - \Delta H_{1,reaction} = \Delta C_p \, (T_2 - T_1)$$

$$\Delta H_{2,reaction} = \Delta H_{1,reaction} + \Delta C_p \, (T_2 - T_1)$$

We define that the reaction enthalpy at T_1 is $\Delta H_{1,reaction}$ and reaction enthalpy at T_2 be $\Delta H_{2,reaction}$ and integrate the left side of the equation as shown above. On the right side though, we have ΔC_p and to proceed with integration, we will assume that ΔC_p is independent of temperature. If all our reactants and products are ideal gases, this is perfectly valid and needs no discussion. But for real gases, this will be an approximation. However, the difference in the heat capacities between the reactants and products are weakly dependent on temperature, even when the C_p values are dependent on temperature. Thus, often, this assumption is reasonable, and with this caution, we proceed to integrate on the right side of the equation. Upon further rearrangement, we see that the heat of reaction at any temperature can be calculated from the heat reaction measured at one temperature, and by knowing the value of ΔC_p, our goal was achieved. We recognize again that these heats of reactions are at the two temperatures of interest.

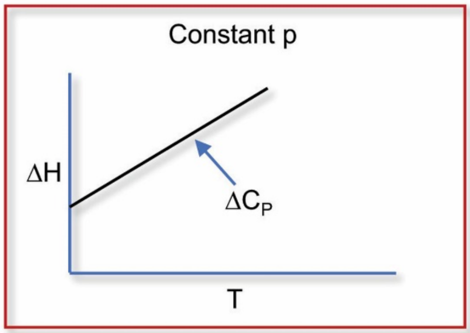

Figure 12.4 Plot of the heat of reaction as a function of temperature for any reaction involving ideal gases. This plot is a good approximation for the reactions of real gases, particularly if the temperature interval is small enough that ΔC_p is independent of temperature over the interval.

A plot of ΔH versus temperature is shown in Figure 12.4 for the case $\Delta C_p > 0$, and independent of temperature. The slope will be negative if $\Delta C_p < 0$, and the line will be a curve if ΔC_p is a function of temperature, but the integration we performed earlier will no longer be valid in the last case. With these details in mind, we can use the above plot to calculate the heat of the reaction at various other temperatures. The plot itself is constructed using measurements at few temperatures, with care being exercised regarding the above details about the heat capacity changes.

Example 12.4

Given the value of heat of reaction of methane with oxygen at room temperature is -891.8 kJ/mol at 298.15 K, calculate the heat of the reaction at 500 ˚C (Cp/J mol^{-1} K^{-1}: heat capacities of methane, 35.69; oxygen, 29.38; water vapor, 37.47; carbon dioxide, 36.94, respectively but assume that the temperature dependence of the heat capacities is negligible).

$$CH_4 + 2O_2 \rightleftarrows 2H_2O + CO_2$$

$$\Delta H_{2,reaction} = \Delta H_{1,reaction} + \Delta C_p \, (T_2 - T_1)$$

Given the above values of Cp, we get the enthalpy of the reaction at 500 ˚C, as follows.

$$\Delta H_{500^\circ C} = -891.8 \frac{\mathrm{kJ}}{\mathrm{mol}} + (37.47 + 36.94 - 35.69 - 29.38)(500 + 273.15 - 298.15) = -887.37 \, kJ/mol$$

The answer makes sense because it has the correct sign, correct units and its value is less than at room temperature. This decrease is because the products have a higher heat capacity than the reactants, and hence some enthalpy is used in raising their temperature.

12.3 Standard Enthalpies

In proceeding further, we need to define the molar enthalpy and the standard molar enthalpy for any substance. Standard molar enthalpy is simply the enthalpy of a mole of a pure substance in its standard state at 1 atm pressure and temperature T. We can use the standard state as the most common, stable form. For example, the standard state of carbon is graphite but not diamond, and the standard state of water is liquid water and so on. The standard state of water is liquid, not ice or steam, and the standard state of sulfur is rhombic crystalline form and not the others. We write the standard enthalpy of a substance ($\bar{H}^o$), as follows.

$$\bar{H}^o\ (1\ atm, T)\ \ in\ their\ standard\ form$$

The degree symbol represents that the value is at 1 atm, and the bar represents that it is molar enthalpy in its standard state. The temperature is to be explicitly announced. Because enthalpy is a function of temperature, as we recognized earlier, and it is important to specify the temperature at which the standard enthalpies are computed. By knowing the heat capacities of substances and enthalpy at one temperature, we can calculate standard molar enthalpies at other temperatures.

On the other hand, we recognize that enthalpy has only a weak dependence on pressure, and enthalpy measured at 1 atm can be extrapolated to other pressures that are reasonably comparable to the atmospheric pressure. Thus, all our enthalpies are to be reported at conditions of the standard state of aggregation, standard pressure, and temperature. These values can then be used to calculate the heats of reactions of other reactions. But first, we need to define the heats of formation of compounds to proceed.

12.4 Heats of the Solution, Dilution, etc.,

These are the heats of the corresponding physical processes of dissolution, dilution, and so on, at 1 atm and specified temperatures. However, we recognize that any amount of solute and solvent can be chosen, if their mole numbers are exactly specified, and the dissolution is complete. The heat of dilution differs from that of the solution in that we do not start with a solution of known composition and then add a known amount of solvent to dilute it. These are illustrated below.

$$1\ mol\ H_2SO_4\ (liquid) + 2\ mol\ H_2O(liquid) \rightarrow Aqueous\ H_2SO_4\ (liquid) \qquad (\Delta H_{solution} = \Delta H)$$

$$Aqueou\ H_2SO_4\ (liquid) + 1\ mol\ H_2O(liquid) \rightarrow Aqueous\ H_2SO_4\ (liquid) \qquad (\Delta H_{dilution} = \Delta H)$$

$$Aqueou\ H_2SO_4\ (liquid) + 5\ mol\ H_2O(liquid) \rightarrow Aqueous\ H_2SO_4\ (liquid) \qquad (\Delta H_{dilution} = \Delta H)$$

12.5 Heats of Formation and Heat of a Reaction

The heat of reaction where a substance is formed as the only product from its standard elemental forms is the heat of formation of that substance. For example, the heat of reaction of water, when one mole of water is the sole product produced from hydrogen and oxygen, where all the substances are in their respective standard states, and this is the heat of formation or enthalpy of formation of water. Thus, we can write the following chemical equation to produce water from hydrogen and oxygen and estimate its heat of formation.

$$\left(\frac{1}{2}\right) O_2\ (gas) + H_2(gas) \rightarrow H_2O\ (liquid) + \Delta H_f$$

$$\Delta H_f(H_2O, water) = H\ (H_2O, liquid) - H\ ((\frac{1}{2})O_2, gas) - H\ (H_2, gas)$$

We recognize that the heats of formation of elements are set to zero, as this simplifies all our calculations. Using the heats of formation of elements of reactants and products, we can calculate the heat of a new reaction, without ever doing that exact experiment. This is a powerful tool, as we can predict heats of reactions, as long as we know the heats of formation of the individual chemicals participating in the reaction. Thus, tables of heats of formation are often used to calculate the heats of reactions of interest, even without making a measurement.

Example 12.5

Express the heat of reaction of the reduction of aluminum oxide in terms of the heats of formation of the reactants and products. Also, write the enthalpies of all compounds in terms of the enthalpies of the corresponding elements.

$$2\,Al\,(solid) + (\frac{3}{2})O_2(gas) \rightarrow Al_2O_3\,(solid) + \Delta H_f$$

$$\Delta H_f(Al_2O_3, solid) = H\,(Al_2O_3\,, solid) - \;H\,(2Al, solid) - H\,(O_2, gas)$$

$$\Delta H = H\,(2Al, solid) + H\,(3H_2O, liquid) - H\,(Al_2O_3, solid) - H\,(3H_2, gas)$$

In the above equation, the enthalpies of water and aluminum oxide can be written in terms of enthalpies of formation of the compounds and enthalpies of the corresponding elements, as following.

$$\Delta H \;= H\,(2Al, solid) + 3\,\Delta H_f(H_2O, water) + 3H\left(\left(\frac{1}{2}\right)O_2\;gas\right) + 3H\,(H_2, gas) - \Delta H_f(Al_2O_3, solid)$$
$$-\;H\,(2Al, solid) - H\,((\frac{3}{2})O_2, gas) - H\,(3H_2, gas)$$

$$\Delta H = 3\,\Delta H_f(H_2O, water) - \Delta H_f(Al_2O_3, solid)$$

Thus, we see that the enthalpies of elements are canceled out, and the heat of reaction is expressed only in terms of the heats of formation of compounds.

Thus, enthalpies of elements can be set to any value. Setting them to zero is convenient and reduces the extent of algebraic accounting of calculating the heats of formation. Some heats of formation of compounds at 25 ˚C and 1 atm are given in Table 12.1. We recognize that the units include per mole, as per our definition of the heats of formation.

Table 12.1 Enthalpies of formation of a few substances at 25 ˚C, 1 atm.

Compound	*Formula*	*ΔH_f (kJ/mol)*
Acetone	C_3H_6	-248
Acetylene	C_2H_2	227
Ammonia	NH_3	-46
Ammonium nitrate	NH_4NO_3	-366
Benzene	C_6H_6	-49
Water	H_2O	-242
Carbon dioxide	CO_2	-394
Methane	CH_4	-74.8

12.6 Heats of Combustion

The heat released when one mole of a pure compound in its standard form is combusted with excess elemental oxygen to form its corresponding ultimate oxidation products is the heat of combustion. The heats of combustion are very useful experimental values because we can use them to generate heats of formation of compounds without having to measure them directly from their elemental states. Measuring the heats of formation of most compounds is quite challenging or even impossible because the corresponding chemical reactions from the elements may not occur at all. For example, imagine measuring the heat of the formation of cholesterol directly by combining the corresponding elements to form the compound. There is no such known reaction on earth, but this does not stop us from getting an accurate value of its heat of formation, using the heats of combustion, as described below.

Example 12.6

The heat of combustion of cholesterol is the heat released by its complete combustion in oxygen to produce water and carbon dioxide, as the sole products.

$$C_{27}\,H_{46}\,O\ (solid) + \ excess\ O_2\ (gas) \rightarrow 23H_2O\ (liquid) + 27CO_2 + \Delta H_{combustion}$$

In this manner, we can obtain heats of combustions of various compounds and then use them to calculate the heats of formation of other compounds. For example, the heat of formation of cholesterol is obtained by recognizing that the molar enthalpies of elements are zero and by using the heats of formation of water and carbon dioxide, as following.

$$H\ (C_{27}\,H_{46}\,O\ (solid)) + H\ (excess\ O_2\ (gas)) - H\ \big(23H_2O\ (liquid)\big) - H(27CO_2) = \Delta H_{combustion}$$

$$H\ (C_{27}\,H_{46}\,O\ (solid)) = 0 + H\ \big(23H_2O\ (liquid)\big) + H(27CO_2) + \Delta H_{combustion}$$

Thus, by measuring the heat of combustion of cholesterol and knowing the heats of formation of water and carbon dioxide, we can easily obtain the heat of formation of cholesterol, which is a much easier proposition than measuring the heat of reaction of preparing cholesterol from its constituent elements. The convenience of setting the enthalpies of elementals to zero is also very clear.

The heats of combustion of a few substances are listed in Table 12.2 and a close examination of the data indicate the high enthalpy content of octane while the biofuel, ethanol, has a much lower enthalpy per mol of the substance. The data also reveal that propane does not have as much enthalpy per mole as octane. These and related data are highly valuable to calculate the heats of reactions of numerous cases.

Table 12.2 Heats of combustion of a few substances at 25 ˚C, 1 atm.

Compound	*Formula*	*ΔH_c (kJ/mol)*
Acetone	C_3H_6	1790
Acetylene	C_2H_2	1300
Ammonia	NH_3	393
Benzene	C_6H_6	3268
Carbon monoxide	CO	283
Ethanol	C_2H_6O	1367
Methane	CH_4	891
Methanol	CH_3OH	726
Octane	C_8H_{18}	5470
Propane	H_2O	2220

12.7 Hess' Law

Chemical reactions have additional steps when compared to the physical processes, and these convert our system from a finite initial state to a finite final state with the potential to change the number of moles and chemical structures. Thus, the enthalpy change due to this transformation is independent of the path we take from the initial state to the final state. That is, the fact that enthalpy is a state function allows us to estimate the heat of reaction of interest quite readily from the heats of reactions of certain related reactions that connect the initial and final states. The law states that the heat of reaction of a chemical reaction of interest will be the same irrespective of, if one step is used or a series of steps are used to convert the reactants to products. That is, we can construct an alternate path where the reactants of interest are completely converted to the desired products via a series of reactions where the heats of reactions of each of these steps are already known. The law is stated by the following mathematical relation and illustrated in the following plot (Figure 10.16).

$$\Delta H_{reaction} = \sum_{1}^{n} \Delta H_{ith\ step}$$

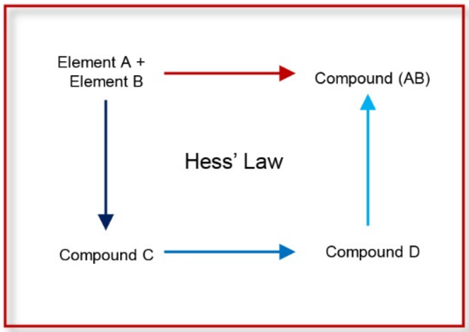

Figure 12.5 Hess' law of heats of reactions from elements or by a multi-step method. The initial and final states of a chemical transformation can be connected by alternate paths. Thus, the enthalpy change of a given reaction can be written in terms of the enthalpy changes of a series of chemical reactions where the enthalpies of each of these steps are known. This is because enthalpy is a state function, and the enthalpies are algebraic. This law is illustrated by the two distinct paths shown.

Thus, by knowing the standard enthalpies of certain reactions, we can compute the reaction enthalpies of specific steps and when these are summed over an appropriate sequence, we obtain the heat of reaction of an unknown chemical reaction or heat of a reaction of a known reaction without having to measure it directly. Thus, Hess' law is of immense value in calorimetry.

Example 12.7

Calculate the heat of reaction of the following reaction,

$$C\ (graphite) + O_2(gas) \rightarrow CO_2(gas) \qquad (\Delta H = ?\ kJ/mol)$$

Using the heats of reactions of the following:

$$C\ (graphite) + (1/2)O_2(gas) \rightarrow CO(gas) \qquad (\Delta H = \ -110.5\ kJ/mol)$$

$$CO\ (gas) + (1/2)O_2(gas) \rightarrow CO_2(gas) \qquad (\Delta H = \ -283.0\ kJ/mol)$$

$$C\ (graphite) + O_2(gas) \rightarrow CO_2(gas) \qquad (\Delta H = ?\ kJ/mol)$$

When we sum the above two reactions, the product CO in the first reaction is used as the reactant in the second reaction, and hence, it cancels off when we sum the two reactions. Then, the heats of reactions of the above two reactions are also summed to get the heat of reaction of the first reaction. For example, -110.5 kJ/mol -283.0 kJ/mol = -393.5 kJ/mol, the heat of reaction of graphite oxidation to carbon dioxide. Thus, we have constructed a two-step process and used this sequence to obtain the heat of reaction of the unknown. These reactions are also combustion reactions, and they are amenable to calorimetric measurements.

One wonderful extension of Hess' law is that it can be applied to all state functions, not just enthalpy, and hence, in future chapters, we will come across several other state functions of chemical reactions, and we can apply this law to all those state functions as well. Thus, this law has a very high utility in the thermodynamics of chemical reactions or physical processes, for that matter.

12.8 Bond Energies and Bond Enthalpies

Bond energies and bond enthalpies are of paramount importance for chemical applications, and they are measured experimentally by different methods, but calorimetry continues to lead the pack. For example, the bond energy of an oxygen molecule is equal to the heat of the reaction where two oxygen atoms are produced from one molecule of oxygen. Similar reactions can be written to determine the bond energies, but we must be careful to recognize that not all bonds are created equal unless they are chemically equivalent. Thus, the geometry of the molecule and the status of the bond in question are important in determining the bond energy.

Example 12.8

How is bond energy determined from heats of reaction for oxygen dissociation, water decomposition into hydrogen atoms and oxygen atoms and for the decomposition of methane into carbon and hydrogen atoms?

Consider the first case of the dissociation of the oxygen molecule into its constituent atoms, given below.

$$O_2(gas) \rightarrow 2O(gas) \qquad (\Delta H_{bond\ enthalpy} = \Delta H_{reaction})$$

The heat absorbed during this reaction or the heat of reaction is used to break the O-O bond, and hence its bond enthalpy is one half of the enthalpy of this reaction. Now consider the next reaction of water dissociation into hydrogen and oxygen atoms.

$$H_2O\ (liquid) \rightarrow 2H(gas) + O(gas) \qquad (2\ \Delta H_{bond\ enthalpy} = \Delta H_{reaction})$$

Here, the enthalpy of the reaction is used to break two O-H bonds which are identical and hence, bond enthalpy is one half the reaction enthalpy. Now consider the last and final example where found equivalent bonds are broken to produce hydrogen atoms and carbon atoms. All four C-H bonds are identical and hence, the bond enthalpy is one quarter the reaction enthalpy.

$$CH_4\ (gas) \rightarrow 4H(gas) + C(graphite) \qquad (4\ \Delta H_{bond\ enthalpy} = \Delta H_{reaction})$$

Then, bond energies are obtained from the bond enthalpies, through the standard thermodynamic relation, as shown below with the ideal gas approximation.

$$\text{Bond energy} = \Delta \mathrm{U}_{bond\ energy} = \Delta \mathrm{H}_{bond\ enthalpy} - \Delta(\mathrm{pV}) = \Delta \mathrm{H}_{bond\ enthalpy} - \Delta \mathrm{n}_{reaction}\ \mathrm{R\ T}$$

We also find that chemical reactions can be exothermic or endothermic, exoenthalpic, or endo enthalpic. Measurements of these quantities have shown that neither internal energy nor enthalpy give us the ability to predict if a chemical reaction occurs spontaneously or its natural direction of progress.

That is, a chemical reaction can occur even if the internal energy of the system is increased or decreased and similarly, a chemical reaction can occur if enthalpy increases or decreases. The often-misused argument that a chemical reaction occurs because it decreases the energy of the system is simply not true, if that energy is U or H. Thus, our quest to find the property of the system that is responsible for driving the chemical reaction forward continues into the next chapters. There, we will ask the question, can entropy predict if a given reaction occurs, if yes, we want to know what would be the natural direction of the chemical reaction?

Table 12.3 Bond energies of a few examples

Bond	*Bond Energy (kJ/mol)*	*Bond*	*Bond Energy (kJ/mol)*
C-C	347	H-Cl	427
C=C	614	H-Br	363
C≡C	839	H-I	295
H-H	432	C-H	413
H-F	565	O-H	467

12.9 Molecular Interpretation

The measurement of enthalpy of a chemical reaction is a practical one and provides the convenience of keeping the pressure constant while the process takes place. Thus, most of the calorimetric measurements are preferred under these conditions, and modern calorimetry is almost entirely done under these conditions.

Extending the law of conservation energy, we note that the energy absorbed or released during a chemical reaction is also conserved, and one form of energy (chemical energy) may be converted into another form (q, w) and hence, heats of reactions or enthalpies of reactions and enthalpies of formation are important. That is when bonds are broken energy is required and when bonds are formed energy is released. When these occur under constant pressure conditions, they contribute to enthalpy changes. Thus, heats of reactions provide unique insight into the molecular details of the substance under investigation. Indeed, bond enthalpies and bond energies are measured this way, which are of daily use in chemistry.

Like a chemical reaction, physical processes such as dissolution, dilution, and combustion also involve enthalpy changes, when they are carried out under constant pressure conditions. These are essential in completely describing the state of the system and monitor the energy conversions during chemical reactions. They also reflect on the interparticle interactions and provide a unique insight into this molecular window.

12.10 Applications in Daily Life

In addition, most of the industrial processes of our culture require energy, often in the form of enthalpy, and hence, this thermodynamic attribute is of primary importance. Finally, we now know that we can produce work at the expense of some other form of energy such as heat, and under constant pressure conditions, it is the enthalpy change that is being used. Thus, only imagination may limit discovering the roles of enthalpy in our daily lives.

12.11 Key points

1. The heat of reaction is the enthalpy change when a chemical reaction occurs under constant pressure conditions.
2. The heat of reaction is a function of temperature and depends on the change in the C_p values of the products and reactants.
3. The bond energies and bond enthalpies are directly measurable by calorimetric methods but these two are related through the equation of state. An ideal gas approximation was used here.
4. Neither U nor H is a useful predictor of the spontaneity of a chemical reaction. That is, saying that a chemical reaction occurs because the energy of the system decreases is just not true if that energy is either U or H. So, we next look to entropy and test if it can predict if a given chemical occurs spontaneously or not.

12.12 New Terms and Units

$$q_p = \Delta\mathrm{H} = (\text{specific heat} \times \text{mass})\,(T_2 - T_1) \qquad \Delta\mathrm{H} = \Delta\mathrm{U} + \Delta(\mathrm{nRT}) = \Delta\mathrm{U} + \Delta\mathrm{n\,RT}$$

$$\Delta\mathrm{H} = q_p = H_{products} - H_{reactants} \qquad \Delta H_{2,reaction} = \Delta H_{1,reaction} + \Delta C_p\,(T_2 - T_1)$$

$$\Delta H_{reaction} = \sum_1^n \Delta H_{ith\ step}$$

$$\Delta\mathrm{U}_{bond\ energy} = \Delta\mathrm{H}_{bond\ enthalpy} - \Delta(\mathrm{pV}) = \Delta\mathrm{H}_{bond\ enthalpy} - \Delta\mathrm{n}_{reaction}\,\mathrm{R\,T}$$

12.13 Self Reflection

1. Find three examples of endothermic chemical reactions, other than the ones given here, and three examples of endothermic physical processes.
2. Given the space of your dorm, discover examples of heat capacities at constant pressure and constant volume.
3. When a chemical reaction releases enthalpy, what is the origin of the energy released (Hint: the law of conservation of energy, first law)? Similarly, when energy is absorbed during the reaction where does it go?
4. When a cube of sugar is burnt in oxygen in a bomb calorimeter, 1000 J of heat was released. What is the change in the mass due to the chemical reaction?
5. Considering that all energy released from burning fossil fuels is warming the planet as a single cause, what is the average heat capacity of the planet? This is kind of justified because temperature of the planet has been stable until about a hundred years ago over a long period.
6. How would you propose to mitigate global warming, based on your knowledge of thermodynamics?

12.14 Further Reading

1. https://ocw.mit.edu/courses/chemistry/5-60-thermodynamics-kinetics-spring-2008/video-lectures/lecture-4-enthalpy/

2. https://ocw.mit.edu/high-school/chemistry/exam-prep/reactions/thermodynamics/heat-of-formation/

12.15 Self Tests

1. During a chemical reaction at constant volume, 2.5 kJ of heat was liberated per mol. There was no change in pressure as the reaction progressed. During an isothermal reaction what is ΔH for the reaction?

   a. -2.5 kJ

   b. +2.5 kJ

   c. 0 kJ

   d. -2.5 kJ/mol

2. True or False? The spontaneity of a chemical reaction can be predicted if the enthalpy (H) and energy (U) are both known.

   a. True

   b. False

3. True or False? The heats of formation of elements are equal to zero.

   a. True

   b. False

4. A constant pressure calorimeter can be used to calculate:

   a. change in temperature

   b. heats of reaction

   c. qv

   d. all of the above

5. The ________ is the enthalpy change when a chemical reaction occurs under constant pressure conditions.

   a. heat capacity

   b. internal energy

   c. heat of reaction

   d. none of the above

6. The enthalpy of a reaction is given as

   a. energy released when a reaction occurs

   b. $= H_{reactants} - H_{produts}$

   c. $= H_{products} - H_{reactants}$

   d. none of the above

7. The heat released into the surroudnings or gained during a reaction at constant pressure is

   a. heat capacity of the system

   b. change in the internal energy

   c. heat released during the reaction

   d. $\Delta\text{H} = (\text{specific heat} \times \text{mass})\,(T_2 - T_1)$

   e. none of the above

8. For the reaction: Fe_2O_3 (solid) + $3H_2$ (gas) → 2Fe (solid) + $3H_2O$ (liquid) + ΔH, q_p is

a. $q_p = (2H_{Fe,solid} + 3H_{H_20,liquid}) - (H_{Fe_2O_3,solid} + 3H_{H_2,gas})$

b. $q_p = (2H_{Fe,solid} + 2H_{H_20,liquid}) - (H_{Fe_2O_3,solid} + 3H_{H_2,gas})$

c. $q_p = (2H_{Fe,solid} + 3H_{H_20,liquid}) - (H_{Fe_2O_3,solid} + 2H_{H_2,gas})$

d. $q_p = \left(H_{Fe_2O_3,solid} + 3H_{H_2,gas}\right) - (2H_{Fe,solid} + 3H_{H_20,liquid})$

e. none of the above

9. The reaction enthalpies (ΔH) and reaction internal energies (ΔU) of chemical reactions are related via the change in mole numbers (Δn) as:

a. $\Delta H = \Delta U - \Delta(nRT) = \Delta U - \Delta n\ R$
b. $\Delta U = \Delta H + \Delta(nRT) = \Delta U + \Delta n\ R$

c. $\Delta H = \Delta U + \Delta(nRT) = \Delta U + \Delta n\ R$

d. $\Delta H = \Delta U + \Delta(nRT) = \Delta U + \Delta n\ RT$

e. none of the above

10. For exothermic reactions

a. $\Delta H > 0$
b. $\Delta U > 0$

c. $\Delta H = \Delta U$

d. $\Delta H < 0$

e. none of the above

11. For endothermic reactions

a. $\Delta H > 0$
b. $\Delta U > 0$

c. $\Delta H = \Delta U$

d. $\Delta H < 0$

e. none of the above

12. Temperature dependence of heat reaction is given by

a. $\Delta H_{1,,reaction} = \Delta H_{1,reaction} + \Delta C_p\ (T_2 - T_1)$
b. $\Delta H_{1,reaction} = \Delta H_{2,reaction} + \Delta C_p\ (T_2 - T_1)$

c. $\Delta H_{2,reaction} = \Delta H_{1,reaction} + \Delta C_p\ (T_2 - T_1)$

d. $\Delta H_{2,reaction} = \Delta H_{1,reaction} + \Delta C_p\ (T_2 - T_1)$

e. none of the above

13. The standard enthalpy of a substance at any temperature T is defined as

a. $\bar{U}^o\ (1\ atm, T)\ \ in\ their\ standard\ form$

b. $\bar{H}^o\ (1\ atm,\ room\ temperature)\ \ in\ their\ standard\ form$

c. $\bar{H}^o\ (1\ atm)\ \ in\ their\ standard\ form$
d. $\bar{H}^o\ (1\ atm, T)\ \ in\ their\ standard\ form$

e. none of the above

14. Heat of formation of water is defined as

a. $\Delta H_f(H_2O, water) = H\ (H_2O, liquid) - H\ ((\frac{1}{2})O_2, gas) - H\ (H_2, gas)$

b. $\Delta H_f(H_2O, water) = U\ (H_2O, liquid) - H\ ((\frac{1}{2})O_2, gas) - H\ (H_2, gas)$

c. $\Delta H_f(H_2O, water) = H\ (H_2O, liquid) + H\ ((\frac{1}{2})O_2, gas) - H\ (H_2, gas)$
d. $\Delta H_f(H_2O, water) = H\ (H_2O, liquid) + H\ ((\frac{1}{2})O_2, gas) + H\ (H_2, gas)$

e. none of the above

15. The Hess law of heat of reaction is defined as

a. $\Delta U_{reaction} = \sum_1^n \Delta U_{ith\ step}$

b. $\Delta H_{reaction} = \sum_1^n \Delta H_{ith\ step}$

c. $\Delta H_{reaction} = \sum_1^n \Delta U_{ith\ step}$
d. $\Delta U_{reaction} = \sum_1^n \Delta H_{ith\ step}$

e. none of the above

16. The following expression is used to estimate the bond energy from the bond enthalpy measurements of a gaseous reaction in a constant pressure calorimeter, at temperature T

a. $\Delta \mathrm{H}_{bond\ energy} = \Delta \mathrm{H}_{bond\ enthalpy} - \Delta(\mathrm{pV}) = \Delta \mathrm{H}_{bond\ enthalpy} - \Delta \mathrm{n}_{reaction}\ \mathrm{R\,T}$

b. $\Delta \mathrm{U}_{bond\ energy} = \Delta \mathrm{U}_{bond\ enthalpy} - \Delta(\mathrm{pV}) = \Delta \mathrm{H}_{bond\ enthalpy} - \Delta \mathrm{n}_{reaction}\ \mathrm{R\,T}$

c. $\Delta \mathrm{U}_{bond\ energy} = \Delta \mathrm{H}_{bond\ enthalpy} - \Delta(\mathrm{pV}) = \Delta \mathrm{H}_{bond\ enthalpy} - \Delta \mathrm{n}_{reaction}\ \mathrm{R\,T}$
d.$\Delta \mathrm{U}_{bond\ energy} = \Delta \mathrm{H}_{bond\ enthalpy} - \Delta(\mathrm{pV}) = \Delta \mathrm{H}_{bond\ enthalpy} + \Delta \mathrm{n}_{reaction}\ \mathrm{R\,T}$

e. none of the above

17. Given the value of molar heat of combustion of methane in oxygen at 500 ˚C is $-887.37\ kJ$, the value at room temperature is

a. -891.8 kJ/mol

b. 891.8 kJ/mol

c. -898.8 kJ/mol
d. -991.8 kJ/mol

e. none of the above

18. The molar reaction enthalpy of for the decomposition of methane into hydrogen atoms and carbon atoms is ΔH, the molar bond enthalpy of a C-H bond is

a. -ΔH/4 kJ/mol

b. ΔH/4 kJ/mol

c. ΔH kJ/mol
d. ΔH/2 kJ/mol

e. none of the above

19. The molar heat of enthalpy for the isomerization of A to B is only 25 kcal/mol, the molar energy of the reaction for this reaction is

a. 12.5 kcal/mol

b. 25 kcal/mol

c. can't say

d. none of the above

20. One mole of sulfuric acid as added to two mole of water at room temperature. If the heat liberated is x kcal/mol, the heat of solution is

a. x/2
b. x

c. 2x

d. x^2

e. none of the above

12.16 Self Tests Key

1. d, 2. b, 3. a, 4. d, 5. c, 6. c, 7. d, 8. a, 9. c, 10. d, 11.a, 12, c, 13. d, 14. a, 15. b, 16.c, 17. a, 18. b, 19.b, 20. b

12.17 Problems

1. During a chemical reaction at constant volume, 2.5 kJ of heat was liberated per mol. There was no change in pressure as the reaction progressed, at constant temperature. What is ΔH for the reaction? (Ans. -2.5 kJ/mola
2. A constant volume calorimeter was used to determine the heat released when 1.5 g of sugar was combusted at 25 ˚C in pure oxygen at 1.5 atm pressure. The mass of the calorimeter was 1.5 kg made of metal of specific heat of 2 J/K g which was surrounded by water of 1 L (s= 4.18 J/K g). The temperature rise during the combustion was 0.210 K. Calculate the molar heat of combustion of sugar. (Ans.5,164 kJ/mol)
3. Using the data from the above experiment calculate the molar heat of combustion under constant volume conditions. (Ans. 5,139.3 kJ/mol)
4. Using the heats of formation data for the reactants and products, calculate the heat of reaction of carbon burning in oxygen, at room temperature and 1 atm. (Hf(kJ/mol): water vapor, -241.5; carbon dioxide, -393.5) (Ans. -635 kJ/mol of either product).
5. The bond enthalpy of the O-H bond is 467 kJ/mol at room temperature. What is the heat of reaction of the disproportionation of water into hydrogen atoms and oxygen atoms? (Ans. 934 kJ/mol)
6. The heat of combustion of liquid ethanol at room temperature is -1364 kJ/mol. What is the heat of reaction at 500 K? (Ans. -1379 kJ/mol)
7. The bond energy of the H-H bond is 432 kJ/mol, what is the enthalpy of reaction of its decomposition into hydrogen atoms at this temperature? (Ans. 434.48 kJ/mol)
8. Design an experiment to measure the dissociation energy of carbon dioxide (Use Hess' law).
9. Design an experiment to estimate the bond dissociation energy of molecular iodine using a calorimeter. You may use a catalyst that can dimerize the methyl radicals.
10. How would you determine the binding energy of DNA polymerase to its substrate (double stranded DNA)?

Chapter 13. The Second Law of Thermodynamics

After completing this chapter, you will be able to:

- Recognize the definition of entropy
- Design a Carnot cycle and calculate the reversible cyclic work/heat of this cycle
- Apply the work of isothermal expansion, adiabatic expansion, isothermal compression, and adiabatic compression.
- Proved a general proof for entropy as the state function
- Use entropy as a predictor of the direction of a natural process.

Goals

- Construct the cyclic integrals of work, heat, and dq_{rev}/T for the Carnot cycle and define entropy.
- Prove that entropy is a state function

13.1 Why Study This?

Entropy is a key thermodynamic function. Recognition of entropy as a state function and general proof for this fact is an important milestone in thermodynamics. Entropy plays a key role in the thermodynamics of all systems, and the definition of entropy is considered as the statement of the second law, which is vital to our discussions of chemical reactions and physical processes. The tendency of a natural process to occur is fundamentally due to the increase in the net entropy of the universe, system plus surroundings! Therefore, entropy is a very powerful and important property. Entropy changes of a system alone, during a process, however, are not predictors of a spontaneous process. Analyzing the entropy changes in the system and the surroundings allows us to determine if a given process is spontaneous, and hence, entropy is the first successful predictor of spontaneity. Thus, the discussion of entropy as a state function is a key step in moving forward. This task is of paramount importance for chemists, biologists, physicists, and others, in general. Thus, predicting under what conditions will a chemical reaction or a physical process happens or controlling its direction is of significance. Thus, this chapter is important to make progress toward our quest of understanding the answer to the enquiry, why do chemical reactions occur or how to control them to occur in each direction or in the opposite direction? We will begin with reversible cyclic processes.

13.2 Reversible Cyclic Process

We begin our discovery of entropy as a state function by taking a closer look at a reversible cycle, associated with the transformations of an ideal gas. When the cyclic integral of any property of the system is zero, then that property must be a state function. Thus, we choose a cyclic process for our discussions. Next, we choose reversible cycles, so that we can examine entropy in terms of other state functions. We use an ideal gas because we precisely know its equation of state which will be useful for mathematical transformations of the equations we get. Thus, this cyclic process will also an ideal cycle, and hence, serves as a limiting model to discuss other cyclic processes. We recall that the work and heat terms associated with the isothermal and adiabatic reversible processes are already discussed in the previous sections, and hence these can be readily applied to our reversible cycle.

Our strategy is to show that the cyclic integral of entropy for a reversible cycle consisting of four steps (Figure 13.1) is zero. Then, we show that this result is correct for also irreversible cycles, establishing entropy as a state function. Consider a reversible cyclic process with the four steps, indicated below.

Step 1: Isothermal reversible expansion, which converts the initial state A on the left top corner of the diagram at T_1 to give rise to state B at the top right corner (Figure 13.1). The system is performing work by receiving q from the surroundings, under isothermal conditions. Thus, its internal energy is kept constant during this isothermal transformation.

Step 2: An adiabatic expansion, which converts state B at the top right lower corner to state C, at the lower right corner. Because this is an adiabatic expansion (q = 0), temperature decreases from T_1 to T_2 as it performs work in the surroundings, at the expense of its internal energy. Temperature decreases during this step because the system is producing expansion work adiabatically, at the expense of its internal energy while there is no exchange of q with its surroundings.

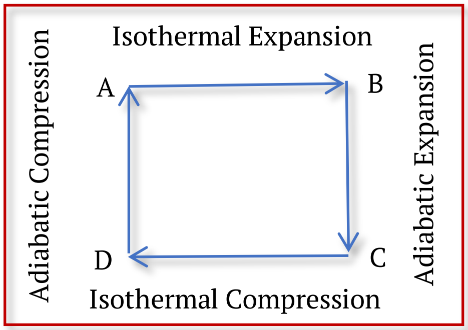

Figure 13.1 An ideal cyclic process consisting of four steps: an isothermal expansion (A to B), adiabatic expansion (B to C), isothermal compression (C to D), and adiabatic compression (D to A) of an ideal gas. The two isothermal processes are carried out at temperatures T_1 and T_2 where $T_1 > T_2$. This is the Carnot cycle which involves two expansion steps followed by two compression steps, and it is a useful tool to define entropy or the mathematical statement of the second law of thermodynamics. Thus, a very important topic to examine.

Step 3: Now, the system travels back toward the initial state via the isothermal compression at temperature T_2 from state C to D (bottom left corner). Since this is an isothermal compression, work is performed while releasing heat into the surroundings. We recall that $T_2 > T_1$, as deduced in step 2, above.

Step 4: Return of the system is completed by bringing it from state D to state A via an adiabatic compression ($q = 0$), which increases its temperature from T_2 to T_1. The temperature increases in this step because work is destroyed in the surroundings during the adiabatic compression, which increases the internal energy of the system raising its temperature back to T_1.

In summary, we have four reversible processes, two isothermal and two adiabatic steps. The isothermal expansion from A to B and the adiabatic expansion from B to C, are during the forward process. The reverse processes consist of isothermal compression from C to D and adiabatic compression from D to A. We could have chosen more steps but that would make it unnecessarily complex and just four steps are sufficient for our discovery of entropy. We recognize that the entire cycle is reversible where each step is reversible, and irreversible cycles will be discussed later.

The reasons for this choice will become clear in a few steps. We will use this reversible cycle to define entropy (S), and then show that $\int_{cycle} dS = 0$ for this reversible cycle. Next, we show that $\int_{cycle} dS = 0$ for any cycle, not just for reversible cycles. Thus, we will finally prove that entropy is a state function.

We emphasize that steps one and three are conducted at different temperatures and that T_1 must be greater than T_2 and this is because T_1 and T_2 are connected by the adiabatic reversible expansion, step 2 during which the system is lifting masses in the surroundings at the expense of its internal energy ($\Delta U < 0$). Similarly, step 4 must raise the temperature from T_2 to T_1 to restore the system to its initial temperature, and this is done by lowering masses in the surroundings during this compression step where the energy is stored in the system as an increase in ΔU.

Thus, while steps one and three are isothermal with the temperature of the system being unaffected, steps two and four are adiabatic and the temperature of the system is changing. Whether the temperature is decreasing or increasing during these latter steps depended on if the process is expansion or compression.

Reversibility of the cycle ensures that there are no permanent changes in the system or the surroundings, and if we run the cycle backwards, the same changes will occur in the reverse direction. The only difference is that the signs of changes will be reversed. With these descriptions of the individual steps of this unique reversible cycle (Carnot cycle), we next proceed to write the expressions for w, q, and ΔU values for each of these four steps. To do that, we will define the pressures and volumes of the ideal gas at each of the four states, A through D, and observe their changes for each step.

13.2.1 The p-V diagram for the Carnot cycle

The entire Carnot cycle can be drawn as a p-V diagram for better recognition of how these variables of the system change as we cycle the system through the four steps. Using the ideal gas, we construct pressure-volume plots for the isothermal and adiabatic steps (Figure 13.2). We choose pressure on the y axis and volume on the X-axis. For the reversible isothermal expansion (step 1), we connect the initial state at p_1 and V_1 with state p_2 and V_2 on the top right, where p_2 is lower than p_1, and V_2 is higher than V_1, both states being at temperature T_1. Next, the expansion continues under adiabatic conditions with an increase in volume and drop in pressure from p_2 V_2 to p_3 V_3. The adiabatic expansion lowers the temperature from T_1 to T_2, with a steep pressure drop, as the volume increases and reaches state p_3 V_3. This completes the first half of the cycle.

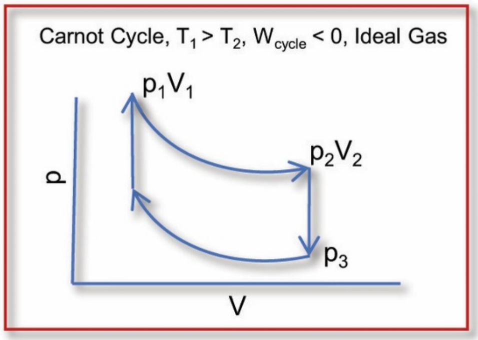

Figure 13.2 Pressure-volume plot for Carnot cycle consisting of steps 1 through 4, where step one is the expansion with increase in volume and decrease in pressure connecting state p_1V_1 to state p_2V_2. The second step continues the expansion further, under adiabatic reversible conditions, with a steeper decrease in pressure and increase in volume converting state p_2V_2 to p_3V_3. The steeper drop in pressure in the send step, when compared to step 1, is due to a drop in temperature during the adiabatic expansion. Steps three and four follow steps 1 and 2 in the reverse direction, through state p_4V_4, back to p_1V_1. Note that these latter two steps run parallel to the first two steps but offset along the y- and x-axes, respectively. The arrows indicate the direction of each step. These steps are reversed when the cycle is reversed.

The journey back to the initial state because this is a cyclic transformation, involves isothermal compression with a decrease in volume (step 3) but an increase in pressure to p_4 and decrease volume to V_4. We recognize that this is Boyle's law, as is step 1, of reversible compression, and this step is parallel to step one but carried out at a lower temperature, T_2. Step four is the adiabatic compression which runs parallel to step two, connecting p_4 V_4 with the initial state p_1V_1. The arrows on the lines indicate the direction of the process. Again, the steep increase in pressure during step 4 is due to adiabatic compression where the temperature increases from T_2 to T_1.

Thus, the pressure-volume plot forms a parallelogram, where each step is curved. The direction of each step is indicated by its arrowhead, and reversal of the cycle requires reversing the direction of each of the four steps. We have started from the initial values of p_1, and V_1 and returned to this original state, and therefore, this is the p-V diagram of a cyclic transformation.

13.2.2 The w, q, and ΔU terms for the Carnot cycle

We already announced that the temperature of the isothermal step one is T_1 and that of step three is T_2 but $T_1 > T_2$, and this is because the adiabatic expansion in step two lowers the temperature of the system. Since these two are isothermal steps, ΔU with these two steps is zero, as shown in Figure 13.3. Thus, applying the first law ($\Delta U= dq + dw$), we deduce that magnitudes of the heat terms for steps one and three are also equal to their corresponding work terms. We will look at this cyclic process and write the w, q, and ΔU terms for all four steps, and then figure out the work of the whole cycle (W_{cycle}, Table 1).

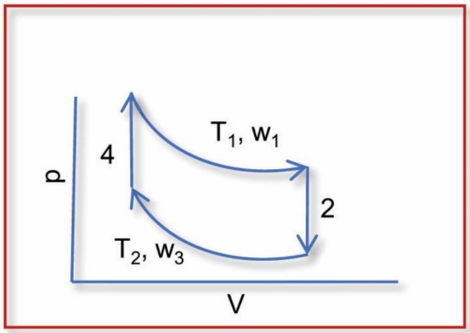

Figure 13.3 Pressure-volume plot for the Carnot cycle, with the corresponding w, and T terms, illustrated for each of the four steps. Steps one and three are isothermal at temperatures T_1 and T_2, and $\Delta U = 0$ for each of them, and hence, the q terms are equal in magnitude to the corresponding work terms, w_1 and w_3, respectively (Table 13.1). Steps two and four are adiabatic and hence, the corresponding q terms are set to 0. Thus, the ΔU terms of these steps are equal to the work terms w_3 and w_4.

For step 1, isothermal expansion, we showed that work (w_1) produced by the ideal gas is $-nRT_1 \ln(V_2/V_1)$, where the final volume is V_2 and the initial volume is V_1. Because this step is isothermal, ΔU is zero, and therefore, applying the first law we conclude that $q = -w_1$.

Table 13.1 The w, q and ΔU terms for the Carnot cycle.

Process	*Work*	*Heat*	*ΔU*
Isothermal expansion	$w_1 = -nRT_1 \ln(V_2/V_1) < 0$	$-w_1$	0
Adiabatic expansion	$W_2 = \Delta U < 0$	0	$C_v(T_2-T_1) < 0$
Isothermal compression	$w_3 = -nRT_2 \ln(V_4/V_3) > 0$	$-w_3$	0
Adiabatic compression	$w_4 = \Delta U > 0$	0	$C_v(T_1-T_2) > 0$

For the second step, the adiabatic expansion, q is zero, and hence, work is equal to ΔU. Since this is a reversible adiabatic expansion, temperature decreases and $\Delta U = C_v(T_2-T_1)$ which is also equal to w_2.

Now, we recognize the second half of the cycle, with isothermal reversible compression in step three, which is like step one, but the volume is decreasing because it is compression. So, the work w_3 is given as $-nRT_2 \ln(V_4/V_3)$. As this is isothermal, ΔU is zero and q is equal to $-w_3$. The last and final step is the adiabatic compression with q equal to zero and w_4 equal to ΔU, which is $C_v (T_1-T_2)$, where T_1 is the final temperature. Then, the system is restored to its initial state.

So, this kind of analysis for each of the four steps is important and we need to recognize the basis for writing the terms for each of the steps. Now we calculate the w, q, and ΔU for the entire cycle, as follows.

13.2.3 Work done in one cycle

As the system passes through the cycle, we can argue that W_{cycle} and q_{cycle} will be simply the sum of the corresponding values of the individual steps. For example, W_{cycle} is given as follows, where the work terms for each of the four steps (w_1, w_2, w_3, and w_4) are summed.

$$W_{cycle} = w_1 + w_2 + w_3 + w_4$$

Writing the values of work for these steps from Table 1, we write the following expression, where the cyclic work is written in terms of n, V, and T terms.

$$W_{cycle} = -n\,R\,T_1 \ln(V_2/V_1) + C_V\,(T_2 - T_1) - n\,R\,T_2 \ln(V_4/V_3) + C_V\,(T_1 - T_2)$$

The work terms for steps two and four, which are adiabatic reversible processes occurring between the same temperatures, cancel, each other out. The remaining terms are the sum of the work terms for the first and the third steps, and taking $-nR$ as common, we get the following expression.

$$W_{cycle} = -n\,R\,[T_1 \ln(V_2/V_1) + T_2 \ln(V_4/V_3)]$$

By recognizing that the volume terms are connected by adiabatic processes, we can equate the ratios of volume terms under the logarithms. The adiabatic steps three and four are connected through their respective temperatures and volumes, from the previous chapter, γ is the ratio C_p/C_V, as following.

$$T_1\,(V_2)^{\gamma-1} = T_2\,(V_3)^{\gamma-1}$$

$$T_1\,(V_1)^{\gamma-1} = T_2\,(V_4)^{\gamma-1}$$

By dividing the first equation by the second, we release the temperature terms and get the relation between the volumes as follows.

$$V_2/V_1 = V_3/V_4$$

Using this relation, we write W_{cycle} from the above equation in a simpler form, as below.

$$W_{cycle} = -n\,R\,[T_1 \ln(V_2/V_1) + T_2 \ln(V_1/V_2)]$$

By inverting the second logarithmic term, we change its sign and take that out as a common term to get the following final expression.

$$W_{cycle} = -\mathrm{n}\,\mathrm{R}\ln(V_2/V_1)\,(T_1 - T_2)$$

We recognize that the equation for the cyclic work depends on the temperature differences between the two isothermal steps and the volume change during the first step, as well as the number of moles of the gas. This is much simpler than we might have envisioned, and this simplification is because the adiabatic steps canceled each other out but they provided a method to simplify the final relation. We analyze this by writing three separate cases.

Example 13.1

Define the standard steps of the Carnot cycle and give the key features for each of the 4 steps.

There are four standard steps, and their key features are:

Step 1: Isothermal reversible expansion; ΔU =0; ΔH = Δ(pV), q>0, w<0, w = -q, w = -nRT1ln(V_2/V_1), ΔS =q/T1

Step 2: Adiabatic reversible expansion; q=0; ΔU = $C_v(T_2-T_1)$, ΔH =ΔU + Δ(pV), w<0, w = ΔU, ΔS =0

Step 3: Isothermal reversible compression; ΔU =0; ΔH =ΔpV, q <0, w >0, w = -q, ΔS =q/T1

Step 4: Adiabatic reversible compression; q=0, ΔU =$C_v(T_2-T_1)$, ΔH =ΔU + Δ(pV), w >0, ΔS= 0

13.2.3.1 Case 1: W_{cycle} when $T_1 = T_2$

The general expression for the W_{cycle} for the Carnot cycle reduces to an interesting limit when the temperatures of isothermal steps one and three are equal.

$$W_{rev,cycle} = 0, \quad T_1 = T_2$$

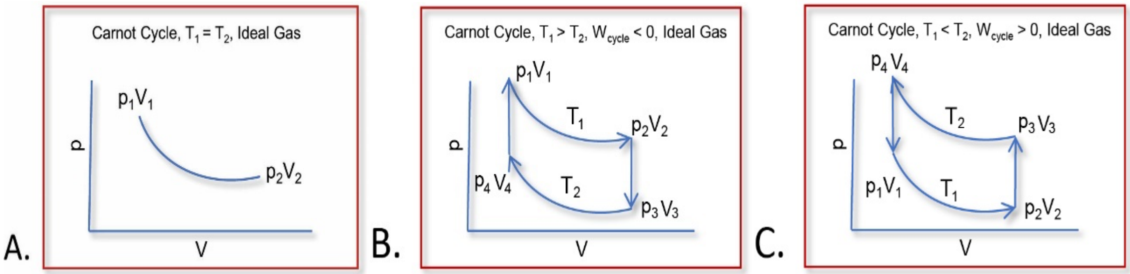
A.
Carnot Cycle, $T_1 = T_2$, Ideal Gas
p
p_1V_1
p_2V_2
V
B.
Carnot Cycle, $T_1 > T_2$, $W_{cycle} < 0$, Ideal Gas
p
p_1V_1
T_1
p_2V_2
p_4V_4
T_2
p_3V_3
V
C.
Carnot Cycle, $T_1 < T_2$, $W_{cycle} > 0$, Ideal Gas
p
p_4V_4
T_2
p_3V_3
p_1V_1
T_1
p_2V_2
V

Figure 13.4 Pressure-volume plot for Carnot cycle under three conditions. A. Case 1: when $T_1 = T_2$. The parallelogram turns into a line with zero area enclosed (W_{cycle}) and the adiabatic steps collapse to points. B. Case 2: when $T_1 > T_2$ and $V_1 < V_2$, the parallelogram has a finite area, and $W_{cycle} < 0$ or masses are raised in the surroundings or cycle produces work in the surroundings. C. Case 3: when $T_1 < T_2$, the parallelogram still encloses a finite area (W_{cycle}) but a net amount of work destroyed in the surroundings.

That is, the two isothermal steps are concurrent and hence, our parallelogram becomes a line, with no area enclosed (Figure 13.4, left). This is because the W_{cycle} equals zero, when $T_1 = T_2$, from the above equation, and the area enclosed is the magnitude of the work for the cycle. Therefore, steps two and four collapses to points. Thus, one of the limiting values of the work for this kind of a cycle is that as the temperatures of the two isothermal steps approach each other, the cyclic work approaches zero.

$$Case\ 1: W_{cycle} = -\mathrm{n\,R}\ln(V_2/V_1)\,(T_1 - T_2) = 0$$

Moving forward, we ask how we maximize the work derived from this cycle, which leads to the second case, discussed below.

13.2.3.2 Case 2: When $T_1 > T_2$ and $V_1 < V_2$

When the expansion is at a higher temperature than the compression ($T_1 > T_2$), as in your automobile engine, and when the first step is expansion ($V_2 > V_1$) then, both terms in the above equation are positive. Thus, $W_{cycle} <0$, the net amount of work appears in the surroundings during each cycle. Your automobile engine is cyclic but not a reversible engine and hence, these arguments are applied here only in a comparative manner. We can construct an imaginary automobile engine that runs this reversible cycle, and these arguments apply quantitatively for such ideal engines.

$$Case\ 2: W_{cycle} = -\mathrm{n\,R}\ln(V_2/V_1)\,(T_1 - T_2) < 0$$

When $T_1 > T_2$, the expansion is taking place at a higher temperature than the compression, producing more work during the expansion but consuming less work during the compression to prepare the system for the next cycle. This is how all heat engines such as automotive or steam engines work, which are not reversible cyclic engines. We note that the area enclosed by the parallelogram is non-zero (Figure 13.4, middle) and it can be measured by simple geometry. Larger the value of T_1-T_2, the greater the work produced in the surroundings.

The modern automobile engines work at higher and higher temperatures, producing more and more work from the same amount of fuel. But this requires special oils to cool the hotter and hotter engines, which is an entirely different problem to deal with. Larger the ratio of V_2/V_1, the greater the work produced in the surroundings but note the logarithmic function of this ratio. Thus, work does not increase or decrease linearly with the volume ratio, but in a logarithmic manner, which has a significant impact on the construction of automobile engines and steam turbines.

Example 13.2

Calculate the work done when 2 moles of gas expand isothermally and reversibly from an initial volume of 200 L to a final volume of 500 L, at 300 K.

$W = -nRT_1 \ln\left(\frac{V_2}{V_1}\right) =-2 * 8.3.03\ \frac{L\ atm}{mol\ K} * 300K \ln\left(\frac{500\ L}{200\ L}\right)$ = - 4565 atm L

13.2.3.3 Case 3: When $T_1 < T_2$ and $V_1 < V_2$

The last possibility we consider is the case when the expansion occurs at a lower temperature than the compression. Examining the above equation for work, we see that T_1-T_2 <0, but $V_2/V_1 > 1$, and the work term will be >0 or a net amount of work appears in the system. Masses will be lowered in the surroundings, at the end of each cycle. This appears to be a wasteful process, but such a cyclic irreversible process is used in refrigeration and hence, highly relevant. The p-V diagram for the original reversible process will still enclose a finite area, but the sign of the work will be positive (Figure 13.4, right). The above three separate cases provide how the work term changes, based on the experimental conditions, in a rational manner.

$$Case\ 3: W_{cycle} = -\mathrm{n\,R}\ln(V_2/V_1)\,(T_1 - T_2) > 0$$

As mentioned earlier, these three cases provide additional insight into the nature of this famous cycle which we will use to define entropy, shortly. Before that, we will examine the q terms for each of the four steps of the Carnot cycle.

13.2.4 Q_{cycle}

We now write $Q_{cycle,}$ just as we wrote W_{cycle} and q_{cycle} is the algebraic sum of the q values for the individual steps of the cycle, as following, where q_1 is for step one, q_2 is for the adiabatic step two, q_3 is for the isothermal step 3 and q_4 is for the adiabatic step 4. The q terms for the adiabatic steps are zero, and we recognize that ΔU =0 for isothermal steps. Hence, heat and work terms for the isothermal steps are equal but opposite in sign, as given by the first law of thermodynamics. Thus, we get the following expression for the heat terms of the Carnot cycle.

$$q_{cycle} = q_1 + 0 + q_2 + \ 0$$

Since ΔU =0 for any cycle, from the first law, we know that q_{cycle} = - W_{cycle}. Thus, we have the following.

$$q_{cycle} \ = -W_{cycle}$$

But we already deduced the relation for the work of this cycle, and hence, we write as follows.

$$q_{cycle} = - \ W_{cycle} = \ \mathrm{n\,R} \ln(V_2/V_1)\,(T_1 - \ T_2)$$

Thus, heat and work terms for the reversible cycle differ only by their sign, and important to keep in mind for problem solving. The values of the heat terms for each of the four steps are also given in Table 1, and we have discussed these values in sufficient detail. In each case, we apply the first law of thermodynamics to obtain the q value, unless it is an adiabatic process where the corresponding q term is zero. Thus, for a reversible cycle, we can state that $(q + w)_{\text{reversible cycle}}$ =0, or this sum is a new state function.

Example 13.3

What are the heat and w terms associate with a Carnot cycle that expands 1 mol of an ideal gas form 10 L to 12 L at a high temperature of 500 K for the first step and a low temperature of 300 K for the third step?

$$q_{cycle} = -w_{cycle} = nRln\left(\frac{V_2}{V_1}\right)(T_1 - T_2) = 1\,mol * 8.31\frac{J}{mol\ K}\ln\left(\frac{10}{12}\right)(500 - 300)K = 303.18\,J$$

Substitution of the corresponding values in the above equation we get the value, and units cancel neatly to give the units of work and heat in J. The answer appears reasonable, has a positive value for q with correct units.

One other detail we need to examine is the energy and enthalpy terms of this cyclic process which are zero, irrespective of whether the cycle is reversible or not because these are state functions. Thus, we obtain two additional relations for the Carnot cycle, which are also valid for any cycle.

$$\Delta U_{cycle} \ = \Delta H_{cycle} \ = 0$$

13.3 Discovery of Entropy

Just as above, we will examine the cyclic integral of the quantity dq/T for this reversible cycle, where dq is heat associated with an infinitesimal step at temperature T. We will see that this exercise leads to the discovery of entropy.

Our strategy is to sum the "q/T" terms for the four steps, and this is straightforward, as we already have the values of q for each of the steps. Using Table 1, we write the following steps for q/T terms for steps 1 through 4, as follows.

$$(q/T)_{reversible\ cycle} = (q_1/T_1) + 0 + (q_2/T_2) + 0$$

Using the isothermal steps, we can write the following using work terms.

$$(q/T)_{reversible\ cycle} = -\ (w_1/T_1) - \ (w_2/T_2)$$

Replacing the work terms with the corresponding volume and temperature terms, we get the following.

$$(q/T)_{reversible\ cycle} = -[[n\ R\ T_1 \ln(V_2/V_1)]/T_1] - \ [[n\ R\ T_2 \ln(V_4/V_3)]/T_2]$$

Upon canceling the temperature terms in the numerator and the denominator in both terms,

$$(q/T)_{reversible\ cycle} = \ -\mathrm{n\ R}\,[\ln(V_2/V_1) + \ln\,(V_4/V_3)]$$

and using the adiabatic relation between the volume terms ($V_2/V_1 = \ V_3/V_4$) as before, we get the final expression as below, which reduces to zero.

$$(q/T)_{reversible\ cycle} = -\mathrm{n}\,\mathrm{R}\,[\ln(V_2/V_1) + \ln(V_1/V_2)] = 0$$

Thus, we can define a new state function entropy (S), as follows and its cyclic integral for the reversible cycle is zero.

$$\mathrm{dS} = (\mathrm{d}q_{reversible}/\mathrm{T})$$

$$\Delta S_{reversible\ cycle} = 0$$

Thus, S appears to be a new state function because its cyclic integral is zero, but what we have shown is that its value is zero only for a reversible cycle. To complete the proof, we need to show that this is the case for any cycle, not just for reversible cycles.

In summary, we defined entropy as $q_{reversible}/T$ and the proof needs to be complete using any cycle, not just a reversible cycle. This will be done in the next chapter, but we continue to the second law of thermodynamics.

13.3.1 The statement of the second law of thermodynamics

From the above discussions, we can simply state that the definition of entropy itself is considered as the second law of thermodynamics, and it is the starting point to derive many thermodynamic functions. We consider the definition of entropy as the second law of thermodynamics, as given below.

$$\mathrm{dS} = \mathrm{d}q_{rev}/T$$

The second law states that a cyclic engine working with a single heat reservoir can't produce a net amount of work in the surroundings or W_{cycle} is ≤ 0, for any cycle operating with a single heat reservoir.

$$\int_{cycle} \frac{dQ}{T} > 0$$

We can dwell on this aspect of the second law by recalling that when the two temperatures are equal for the Carnot cycle, single heat reservoir, then W_{cycle} is zero (Figure 13.5A). Let's consider a reversible cycle (Figure 13.5A). We have a cylinder with a piston containing a certain amount of gas, at a pressure, in equilibrium with a thermal bath. We allow the gas in the cylinder to expand reversibly, raising masses in the surroundings. In the reverse process, we compress it back to its initial state by lowering certain masses in the surroundings, reversibly. The work terms are exactly equal in the two processes but opposite in sign, and the net amount of work derived during the cyclic process is zero. This will be the case for all reversible cycles because the steps are reversible. This is one part of the proof.

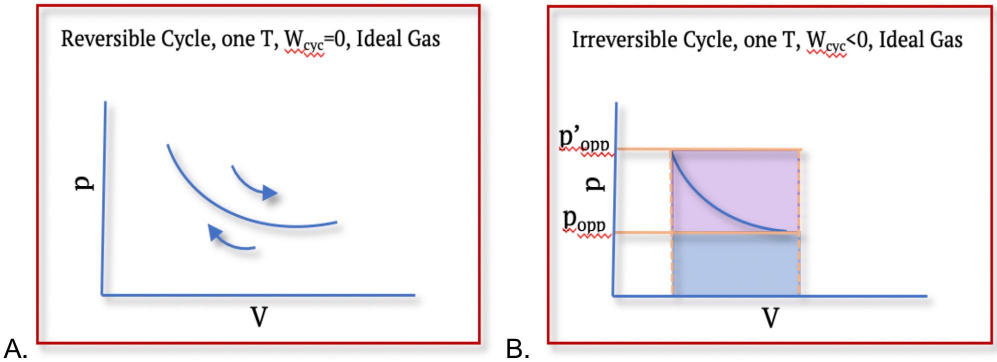

Figure 13.5 A. The work produced or consumed during a reversible cyclic process, reversible cycle with the system in equilibrium with a single heat reservoir. The blue curved arrow represents the reversible isothermal expansion from left to right and during the reverse process, the system moves back from the final state to the initial state. B. Irreversible, one step expansion where the work produced is given by the small blue rectangle, followed by single step compression, where the work needed to traverse back is much greater (larger purple rectangle).

The other part follows when we consider irreversible cycles. The gas will be expanding irreversibly against a pressure $p_{opp} \leq p$, during the first step (Figure 13.5B), and the system is raising masses in the surroundings. The blue rectangle is the area (W) under the p-V curve, and the sign of work for this expansion is negative. In the reverse process, we compress the gas to its initial state using pressure p' ≥ p in one step, but now this takes much more amount of work or larger masses are to be lowered to compress the gas to its initial state (purple rectangle) than produced during the expansion process. We have already calculated these work terms in the previous chapter. Thus, for the irreversible cycle, a net amount of work is destroyed in the surroundings ($W_{cycle} < 0$) during each cycle, and no net amount of work is gained from the system. From the above two discussions, we can conclude the following.

$$W_{cylce} \leq 0 \text{ (single heat reservoir, the second law of thermodynamics)}$$

We immediately recognize, that if you have two or more heat reservoirs then, you will be able to extract a certain amount of work from the system. This aspect is described below, in detail.

13.3.2 The second law and the efficiency of heat to work conversion

Every form of energy can be converted into heat completely. But the conversion of heat into other forms of energy is thermodynamically limited. For example, you have an electrical current passing through a coil producing heat. You can produce almost exactly the amount of heat that is equal to the total electrical energy consumed or that the efficiency for the conversion can be 100%. If we take certain mechanical energy and convert it into heat, we can do what is called the mechanical equivalent of heat, with 100% efficiency. Light also can be converted into heat with 100% efficiency, and we can completely convert all other forms of energy into heat this way. This leads to yet another statement of the second law.

The conversion of heat to other forms of energy, however, is problematic and this is where the second law of thermodynamics sets limits on the efficiency of such conversions, for example. The efficiency of converting heat to work (ε) by a cyclic engine, operating between two heat reservoirs, is given as the net amount of work done in the surroundings divided by the heat withdrawn (q_1) at the higher temperature (T_{high}).

$$\epsilon = w_{cycle}/q_1$$

$$\epsilon = \left[(\mathrm{n\,R} \ln(V_2/V_1)\,(T_{high} - T_{low})\right]/(n\,R\,T_{high} \ln(V_2/V_1))$$

After substituting the expressions for work and q_1, we can cancel n, R, $\ln(V_2/V_1)$ and get a more compact expression, as follows.

$$\epsilon = \left[T_{high} - T_{low}\right]/T_{high}$$

$$\epsilon = 1 - (T_{low}/T_{high})$$

We recognize that T_{high} and T_{low} are the initial and final temperatures of the adiabatic expansion, during which the temperature of the system drops. Therefore, $T_{low} < T_{high}$. Since we are subtracting this ratio from 1, the efficiency must be ≤ 1.

$$\epsilon = \leq 1$$

Two limiting cases are immediately deduced. The efficiency approaches 1 as T_{high} approaches infinity, or as T_{low} approaches 0, and states that the maximum efficiency can't exceed 1, as a thermodynamic limit.

The other limit is that the efficiency equals zero when T_{low} equals T_{high}. In this case, the heat engine operates at one temperature or a single heat reservoir, and its efficiency is zero or it can't produce work. This is the other statement of the second law we discussed.

Example 13.4

What is the efficiency of the Carnot engine working between the two heat reservoirs, the high temperature being at 500 K and the low temperature being 300 K?

Efficiency $= 1 - \frac{T_{low}}{T_{high}} = 1 - \frac{300\,K}{500\,K} = 0.4$

The value seems reasonable as it is less than 1 and also positive.

Indeed, the Carnot engine is an ideal engine, it is the best we can hope for. A real engine, on the other hand, is very likely to have an efficiency less than the ideal engine. The larger the value of T_{high}, the greater will be the efficiency, and the higher the better. Similarly, the lower the value of T_{low}, the greater the efficiency, lower the better. Thus, the second law predicts that the larger the difference between the two temperature reservoirs, the greater would be the efficiency of the engine, and maximum efficiency is obtained when the highest temperature reaches infinity, or the lowest temperature reaches 0 K. These provide limiting conditions for the efficiencies.

Another manifestation of the second law is written as efficiency in terms of q_1 and q_2, as following.

$$\epsilon = \mathrm{W}_{cycle}/q_1$$

Since work terms are proportional to the heat terms, we write the above in terms of heat terms only.

$$\epsilon = \mathrm{q}_{cycle}/q_1$$

Replacing q_{cycle} in terms of q_1 and q_2 we get the expression, where $q_1 > 0$ and $q_2 < 0$.

$$\epsilon = (\mathrm{q}_1 + \mathrm{q}_2)/q_1$$

Upon expansion of the parenthesis, and division, we get the expression that is similar to the one which contained only the temperature terms, earlier.

$$\epsilon = (1 + \mathrm{q}_2/q_1) \text{ when, } q_1 > 0 \text{ and } q_2 < 0$$

Then, the above expression sets an upper limit of 1 for efficiency, when q_2 approaches its highest value of zero or q_1 approaches its highest value of infinity. The system produces work in the surroundings during the cycle, and it cannot release more heat into the surroundings than it absorbed (violation of the first law). This is another statement of the second law, and it sets limits for the efficiency of heat engines.

Example 13.5

What is the efficiency of the Carnot engine that withdraws a heat of 1000 J from a high temperature reservoir and produces 400 J work in the surroundings, during each cycle?

Efficiency $= 1 - \frac{q_{low}}{q_{high}} = 1 + \frac{-600\,J}{1000\,J} = 0.4$

The value seems reasonable as it is less than 1 and also positive.

13.3.3 Thermodynamic scale of temperature

The second law also sets a limit to the lowest temperature that can be achieved in the universe. If T_{low} approaches zero, then the efficiency approaches 1 but temperature <0 can raise the efficiency above 1. Since no engine can have efficiency >1 (violation of the first law), and hence, 0 K is the absolute lower limit to be achieved.

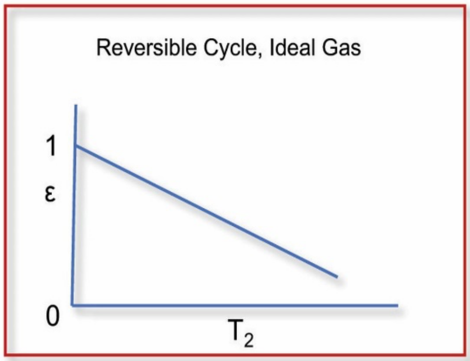

Figure 13.6 Plot of efficiency of the Carnot engine on the Y-axis as a function of the T_{low} on the X-axis for a fixed T_1, and the plot shows that efficiency can't exceed 1 (Y-intercept), unless T_{low} goes below 0 K. Efficiency higher than 100% is prohibited by the first law and the second law prohibits temperatures <0 K.

This situation is illustrated in Figure 13.6 where the efficiency is plotted as a function of T_{low} for a fixed T_{high}. The equation for efficiency shows that the intercept must be one and the slope is negative. As the low temperature approaches zero, efficiency approaches 1. The temperature can't be negative because that will force the efficiency to go above one which is not possible. This is also considered the Second Law of Thermodynamics.

No part of the universe can have a temperature less than zero, if it does then the Carnot engine can have efficiency greater than 1, which is impossible. This defines the absolute 0 kelvin. Therefore, the kelvin scale of temperature is also the thermodynamic scale of temperature. Of course, even obtaining zero K is impossible and so far, we are only able to achieve a few hundred μK.

13.3.4 Graphical illustrations of the Carnot Cycle

To summarize the relationship between the Carnot cycle and specific thermodynamic variables, we plot pairs of a few different variables for this cycle (Figure 13.7). The plot on the right top illustrates how U and V vary for this cycle. States 1 and 3 are given and the two isothermal processes are shown by the horizontal arrows indicating the directions of the path.

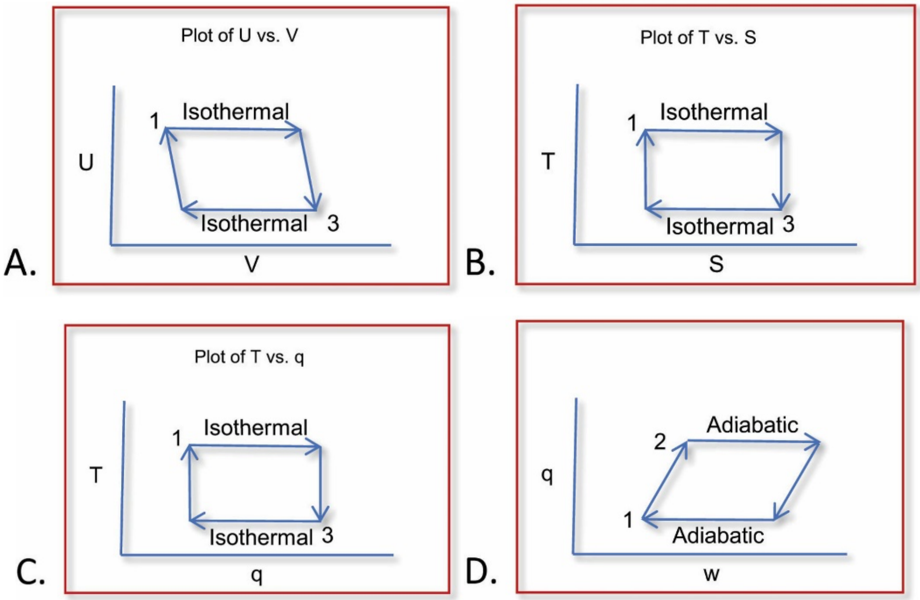

Figure 13.7 Plots of a few thermodynamic functions of the Carnot cycle. A. Plot of U vs V, forming a parallelogram. B. Plot of T vs S, a rectangle. C. Plot of T vs q. D. Plot of q vs w.

During the isothermal expansion, from state 1 to state 2, U is constant, but V is increasing linearly, and hence, it is a line parallel to the X-axis. During the adiabatic expansion, U is decreasing linearly with a further increase in V to reach state 3. The reverse process completes the cycle, and the plot is a parallelogram.

Thus, the Carnot cycle can be represented in many ways but recognizing how the variables change during specific processes of the Carnot cycle is important. For example, T vs S is a rectangle (Figure 13.7B), just as T vs q (Figure 13.7C) while q vs w is another parallelogram (Figure 13.7D). These plots give a more comprehensive understanding of the Carnot cycle.

13.4 General Proof for Entropy as a State Function

We will show that $\int_{cycle} dS = 0$, for any cycle, not just for the Carnot cycle. The proof is provided in two parts. Our strategy is to construct any cyclic process and test if the cyclic integral "$dq_{reversible}/T$" is equal zero. We will assume that for any given cycle "dq/T" is greater than zero, and if that results in an impossible consequence, then we know it must be wrong. Then, we will assume that the cyclic integral is less than zero, and if this results in an impossible consequence, then we know for sure that the third possibility, that the cyclic integral for any cycle must be zero. With this strategy, we move forward.

Our goal is to show that the following is correct for any cycle.

$$\int_{cycle} \frac{dQ_{rev}}{T} = 0$$

13.4.1 Part 1

We assume that this integral is >0 for any cycle.

$$\int_{cycle} \frac{dQ}{T} > 0$$

We have any cycle of choice and call it cycle 1 and let this cycle be coupled with the Carnot cycle, the cycle that we are familiar with. It is ok to couple different cycles because the combination generates a new cycle which also qualifies as a cycle (Figure 13.8).

Figure 13.8 Composite cycle constructed from any cyclic process (cycle 1) and couple it with the Carnot cycle.

The composite cycle is not a reversible cycle, even though the Carnot cycle is a reversible cycle because cycle 1 need not be reversible. Thus, the composite cycle is like any cycle we chose before. Thus, for this composite cycle, we can write the following, from the assumption we made. Let '$dQ_{composite}$' is the infinitesimal heat term for the composite cycle. Then we have the following.

$$\int_{cycle} \frac{dQ_{composite}}{T} > 0$$

We can justify this further. Because the composite cycle has two different cycles embedded in it, we can write this as a sum of two separate terms, where the first term in the integral is from cycle 1, we chose initially, and the second term is for the Carnot cycle.

$$\int_{cycle} \frac{dQ}{T} + \frac{dQ_{carnot}}{T} > 0$$

But we know from the previous chapter that the cyclic integral for the Carnot cycle is zero.

$$\int_{cycle} \frac{dQ_{carnot}}{T} = 0$$

The corresponding work terms for the composite cycle ($W_{composite}$) in terms of the work of cycle 1 (W_{cycle}) and that of Carnot cycle (W_{Carnot}) are related as below.

$$W_{composite} = W_{cycle} + W_{carnot}$$

Now, we adjust W_{carnot} such that its direction and the magnitude be opposite to that of the cycle 1, such that no net amount of work for the composite cycle.

$$W_{composite} = 0$$

This should be feasible from the discussions of the previous chapter where we learned to adjust the work term for the Carnot cycle as we needed. For example, we can adjust the temperatures of the isothermal processes or by controlling the volume or pressure changes of the Carnot cycle, we can control the area enclosed by the Carnot cycle and hence control the magnitude of work (Figure 13.9). We can run the Carnot cycle forward or in the reverse direction, as needed, to make the work of the composite cycle zero.

Figure 13.9 Illustration of Carnot cycles in the reverse direction associated with different amounts of work.

Using the first law, we write work in terms of heat, using the first law of thermodynamics, and substitute $\Delta U = 0$ for any cycle.

$$W_{composite} = -\,Q_{composite} \qquad as\ \Delta U = 0$$

Now, we can write $Q_{composite}$ in terms of individual Q' terms associated with the individual steps of the composite cycle (Q_1, Q_2, Q_3, Q_4,…) for steps 1, 2, 3, 4,….., as following. Thus, sum of these terms must also be equal to zero.

$$Q_{composite} = Q_1 + Q_2 + Q_3 + \cdots = \sum Q_i = 0$$

However, for the composite cycle, the following is true.

$$\int_{cycle} \frac{dQ_{composite}}{T} > 0$$

Now, we write the above integral using the individual Q-terms of each step and their corresponding temperatures, T_1 for step 1, T_2 for step 2, T_3 for step 3,….etc., as following.

$$\int_{cycle} \frac{dQ_{composite}}{T} = \frac{Q_1}{T_1} + \frac{Q_2}{T_2} + \frac{Q_3}{T_3} + \frac{Q_4}{T_4} + \cdots = \sum \frac{Q_i}{T_i} > 0$$

Under what conditions the above integral and $\sum Q_i = 0$ are mathematically valid, simultaneously? We take a closer look at these two conditions, one at a time.

13.4.2 Condition 1: $\sum \boldsymbol{Q_i} = \mathbf{0}$

The sum of the heats of the individual steps of the composite cycle is adjusted to be zero. Therefore, some of these terms are exothermic, some are endothermic while the remaining are adiabatic. Whatever it may be, the Carnot cycle will be adjusted such that W_{cycle} is stet to zero and hence, Q_{cycle} is set to zero, where the negative Q values exactly balance out the positive Q values.

$$Q_{composite} = Q_1 + Q_2 + Q_3 + \cdots = 0$$

All the exothermic processes of the composite cycle balance out all the endothermic processes, and the composite cycle is thermo-neutral. This condition can be satisfied for any cycle when coupled with an appropriate Carnot cycle.

13.4.3 Condition 2: $\sum \frac{\boldsymbol{Q_i}}{\boldsymbol{T_i}} > \mathbf{0}$

The sum of "Q/T" terms of the composite cycle should be greater than zero, where each term is a ratio of the heat to the corresponding temperature for each step of the composite cycle (condition 2). We also recognize that the temperature is in kelvin, and hence, all T values are positive.

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} + \frac{Q_3}{T_3} + \frac{Q_4}{T_4} + \cdots > 0$$

While satisfying condition 1, our composite cycle must also satisfy condition 2, and condition 2 can be satisfied only when positive terms in the sum outweigh the negative terms.

That is, positive Q values are to be divided by lower T values, and negative Q values are to be divided by higher T values. When we divide positive Qs with low T values, we get larger values for the positive terms and when negative Qs are divided with higher temperature values, we get smaller values for the negative terms. Then, the positive terms will outweigh the negative terms, and the sum of all the ratios will be greater than zero.

Thus, we conclude that condition 2 will be satisfied when the positive Qs are associated with processes occurring at lower temperatures and this requires that the system absorbs heat from low temperature surroundings. When the negative Q values are associated with processes occurring at higher T values, heat appears in the surroundings at higher temperatures. This condition has interesting consequences when the composite cycle operates, as follows.

Each time we run the cycle, certain amount of heat flows into the system from the surroundings that are at a lower temperature and certain amount of heat flows from the system into the surroundings at a higher temperature. That is, as the cycle operates, heat flows into the system at a lower temperature and out of the system at a higher temperature. In simple terms, heat flows from a lower temperature source to a higher temperature sink, as the cycle is performed. This is not an issue by itself, because refrigerators work this way moving heat from a low temperature to a higher temperature to keep their contents cold.

However, there is a catch, they consume power to move heat from low temperature to high temperature and for our refrigerators, $W_{cycle} \neq 0$. But we adjusted our composite cycle such that $W_{cycle} = 0$, and hence, our cycle must move heat from low temperature to high temperature without destroying any work in the surroundings, hence this is an impossible task. Therefore, our assumption (see below) must be false.

$$\int_{cycle} \frac{dQ}{T} > 0, in\ correct.$$

This is the first part of our proof it is also the lengthier part. Now, we have two other possibilities, this integral is equal to zero, or it is less than zero.

$$\int_{cycle} \frac{dQ}{T} \leq 0$$

We divide the second part into two cases, reversible cycles and irreversible cycles.

13.4.4 Part 2, Case 1: Reversible cycles

Thus, our assumption now is that for any reversible cycle, the following must be correct.

$$\int_{cycle} \frac{dQ}{T} < 0$$

This case is simple, the proof is like that of the Carnot cycle, but the cycle need not need be Carnot cycle and it can be any cycle that is reversible.

Since this cycle is reversible, we can reverse it and by reversing the cycle and run it backwards. When we reverse the direction of the reversible cycle, the Q, and W values of the individual steps will not change, but all their signs will change. T values do not change either in magnitude or in sign. Then, the above condition will become the following, for the reverse cycle.

$$\int_{cycle} \frac{dQ}{T} > 0$$

When we change all the signs from $-Q_1$ to $+Q_1$ and $+Q_2$ to $-Q_2$, etc., then we can conclude that the sign of the integral should change and now it must be greater than zero. But we just showed that for any cycle, reversible or irreversible, this is not possible. It results in the wrong prediction that heat will flow spontaneously from low temperature to high temperature. Therefore, our assumption that this integral is less than zero for any reversible cycle is also wrong. Then the only remaining possible value for the integral for a reversible cycle is the following.

$$\int_{cycle} \frac{dQ_{reversible}}{T} = 0$$

Since this is a reversible cycle, we can replace the $dQ_{reversible}/T$ with dS, and the cyclic integral is vanishing. We got our proof! Entropy is a state function, after all.

$$\int_{cycle} dS = 0$$

The above is true because we define entropy as $Q_{reversible}/T$ and show that it is a state function. Since entropy is a state function, we also note, its value does not depend on the path taken, reversible or irreversible, its cyclic integral must vanish, regardless.

Let's say that we have an irreversible cycle, and we need to calculate the change in entropy. We will still use the above integral for a reversible cycle, because of the definition of entropy. The change entropy is calculated by constructing a reversible cycle and that integral will vanish. If a change occurs from state one to state two in an irreversible process, then we connect the two states with a reversible process and calculate the entropy change. Even so, we need to examine case II to gain a better understanding of the outcome here.

13.4.5 Part 2, Case 2: Irreversible cycles

For irreversible cycles the values of Q and W will not necessarily be the same. In fact, we showed that isothermal reversible expansion has the largest magnitude for work compared to one step, two step or other finite step expansions. Similarly, we showed that isothermal reversible compression has the lowest magnitude for work when compared to the corresponding irreversible compression processes. Since cyclic integral of $q_{reversible}/T = 0$, we will conclude that the following must be correct for all irreversible cycles.

$$\int_{cycle} \frac{dQ_{irreversible}}{T} \neq 0$$

However, we already showed for any cycle, the following.

$$\int_{cycle} \frac{dQ}{T} \ngeq 0$$

Then, the only possibility left for any irreversible is the following.

$$\int_{cycle} \frac{dQ_{irreversible}}{T} < 0$$

In summary, we showed that entropy is a state function because heat can't spontaneously flow from low temperature to high temperature! To move heat this way, we need to expend work, as in an air conditioning unit or a refrigerator. We could have defined entropy and state that it is a state function as some books do, but the above proof gave us a greater insight into the nature of a natural process and that of entropy. We also showed clearly that the above cyclic integral for all irreversible cycles must be less than zero, a very powerful prediction. Now, we use the above arguments to greater insight into the nature of irreversible process or spontaneous process that we are very much interested in.

13.5 Molecular interpretation

The second law of thermodynamic is a law of practical observations and does not require a molecular basis. However, it should be understandable from molecular principles as well. Since energy can neither be created nor destroyed, the first law states that it is to be conserved in all processes. We may simply convert one form of energy to another but not create it. The first law, however, does not state if it is possible to convert heat to work completely, for example, but we know that all forms of energy can be converted completely into heat. Heat is a manifestation of the random motion of the particles, and if we want to convert this random motion into directed motion or work, then certain conditions apply. Because we need to impose a certain degree of order to convert the disordered motion into an ordered one, and so, the entropy of the particles needs to be reduced. The second law governs this concept and states conditions under which heat can be converted into work and puts limits on the efficiency of work that can be produced from heat. Therefore, entropy and the second law are intrinsically connected at the fundamental level. Entropy and heat are connected at the molecular level as will be described in the next chapter. Heat can't be converted completely to work because some degree of disorder is introduced in the process of producing work. This interpretation provides some insight into the connections between heat, work, and entropy at the fundamental level.

13.6 Applications in daily Life

The thermodynamic laws are foundation stones for our discussions of thermodynamics and their role in real life as well as practical applications or fundamental arguments. The second law, for example, governs the efficiencies of all heat engines and influences the design of planes, trains, and automobiles, or any devices where heat engines are used. It sets the lowest temperature that can be achieved anywhere in the universe. Thus, both in the lab and in life, entropy and the second law are of extreme importance.

Although the application of the second law to chemical reactions is still limited, the application of the concept of entropy is extensively examined in this book, as will be shown in later chapters. Entropy also plays a vital role in real life and entropy driven chemical reactions and physical processes are abundant. A simple expansion of pressurized gas is driven by an increase in entropy. The mixing of sugar cubes in your coffee, in the morning or evening, is driven by entropy, as well as the expansion of the universe. The net entropy of the universe is increasing and hence, the statement that 'entropy is not what it used to be' is correct. There will be numerous examples of entropy changes governing various processes, in the remaining chapters of this book.

13.7 Worked out example

13.8 Key points

1. The definitions of the Carnot cycle, entropy, and the second law are fundamental for the discussions of the thermodynamics of chemical systems.
2. The Carnot cycle is a reversible cycle of expansion and compression involving four distinct steps and four distinct states. The work and heat terms of each of the four steps are obtained by simply applying the first law or the definitions of pV work.
3. During the cycles such as Carnot, we showed that the $(q_{reversible}/T)_{cycle} = \Delta S = 0$.
4. The discussion of the Carnot cycle led us to discover a new state property, entropy.
5. If we show that the above relation in item 3 is true for any cycle, then we have the final proof that entropy is a state function. This will be done in the next chapter.
6. The second law puts certain limits on our attempts to convert heat to work. The maximum efficiency for this conversion can occur only when the high temperature reaches infinity, or the low temperature reaches 0 K.
7. At all other temperatures, the efficiency that can be achieved is precisely predicted by the second law, (<1), and thus, it is of high practical importance.
8. The second law also puts an absolute limit to the lowest temperature in the universe as 0 K.
9. Thus, the thermodynamic scale of temperature is established based on experimental measurements, and this is also the kelvin scale of temperature.

13.9 New terms and units

Cyclic work, reversible cycle, Carnot cycle, the efficiency of a heat engine, entropy, definition of entropy, the second law in various manifestations, and finally the lowest temperature that can be attained as well as the thermodynamic scale of temperature. Entropy has the units of energy/K, and efficiency is a dimensionless quantity.

$$w = -nRT_1\ln(V_2/V_1);\ w = C_v(T_2-T_1);\ q_{cycle} = -W_{cycle} = \mathrm{n\,R}\ln(V_2/V_1)\,(T_1 - T_2)$$

13.10 Self Reflection

1. Discuss the Carnot cycle, given the space of your car.
2. Propose two separate methods to improve the efficiency of your gasoline car or the electric car.
3. Since entropy is defined using q of a reversible process, how can entropy be applied to a real process which is not a reversible one?
4. Considering this planet with its atmosphere as the system and space as its surroundings, what processes in the system are increasing its entropy?
5. Why is the negative temperature on the absolute scale not achievable?
6. Plot H vs U, H vs T, H vs p, and H vs q for the Carnot cycle.

13.11 Further Reading

1. https://ocw.mit.edu/courses/chemistry/5-60-thermodynamics-kinetics-spring-2008/video-lectures/lecture-8-second-law/
2. https://ocw.mit.edu/courses/chemistry/5-60-thermodynamics-kinetics-spring-2008/video-lectures/lecture-10-entropy-and-irreversibility/
3. https://ocw.mit.edu/courses/aeronautics-and-astronautics/16-01-unified-engineering-i-ii-iii-iv-fall-2005-spring-2006/thermo-propulsion/

13.12 Self Tests

1. The Carnot cycle is

a. an ideal irreversible cycle

b. a real, reversible cycle

c. an ideal reversible cycle

d. a real irreversible cycle

e. none of the above

2. The cyclic work done by any Carnot cycle can be

   a. adjustable

   b. >0

   c. <0

   d. zero

   e. all the above

3. Work done in a reversible cycle consisting of isothermal expansion of 1 mole of a gas at 500 K from 1 L to 2 L, adiabatic expansion from 500 to 400 K, followed by an isothermal compression at 400 K with a decrease in volume of 1L, and then adiabatic compression to the initial state is

   a. – (ln 2) (100) K

   b. – ln (2) (830) J

   c. – ln (2) (100) J

   d. - ln (1/2) (830) J

   e. none of these

4. Study of entropy is important because

   a. entropy of the system is a predictor of the spontaneity of a process

   b. entropy of the surroundings is a predictor of the spontaneity of a process

   c. entropy of the system and the surroundings, together, is a predictor of the spontaneity of a process

   d. entropy is never a predictor of spontaneity of a process

   e. none of these

5. The work associated with a cyclic process is

   a. the sum of work associated with the forward processes

   b. the sum of work associated with the reverse processes

   c. the sum of values of work in ‘a’ and ‘c’

   d. the difference in the values of the work of ‘a’ and ‘c’

   e. none of these

6. The Carnot cycle consists of

   a. isothermal expansion, adiabatic expansion and isothermal compression

   b. isothermal compression, adiabatic compression and isothermal expansion

   c. isothermal expansion, adiabatic compression, isothermal expansion and adiabatic expansion

   d. can’t say

   e. none of these

7. The Carnot cycle consists of

   a. isothermal reversible expansion, adiabatic reversible expansion and isothermal reversible compression

   b. isothermal compression, adiabatic reversible compression and isothermal expansion

   c. isothermal reversible expansion, adiabatic reversible expansion, isothermal expansion and adiabatic expansion

d. isothermal reversible expansion, adiabatic reversible expansion, isothermal reversible compression followed by adiabatic reversible expansion

e. none of these

8. The Carnot cycle is

a. an irreversible ideal cycle

b. an irreversible ideal cycle

c. a reversible process by not a cycle

d. an ideal reversible cycle of any combination of processes

e. none of these

9. The cyclic work associated with the Carnot cycle consisting of the isothermal reversible expansion from volume V_1 to V_2, at temperature T_1, adiabatic reversible expansion from volume V_2 to V_3, isothermal reversible compression from volume V_3 to V_4 at temperature T_2 followed by adiabatic reversible compression from volume V_4 to V_1 is

a. $W_{cycle} = \mathrm{n\,R} \ln(V_2/V_1)\,(T_1 - T_2)$

b. $W_{cycle} = -\ln(V_2/V_1)\,(T_1 - T_2)$

c. $W_{cycle} = -\mathrm{n\,R} \ln(V_2/V_1)\,(T_1 - T_2)$

d. $W_{cycle} = -\mathrm{n\,R} \ln(V_1/V_2)\,(T_1 - T_2)$

e. none of these

10. Calculate the cyclic work associated with a Carnot cycle when 1 mol of an ideal gas expands from 2 to 3 L at constant temperature 500 K, followed by adiabatic expansion, then isothermal compression from 5 to 3 L at constant temperature of 300 K.

a. approximately 673 L atm/mol.K

b. <0

c. > 673 L atm/mol.K

d. = 673 joules

e. none of these

11. The work associated with a Carnot cycle when the high temperature and the low temperature reservoirs are at the same temperature is

a. zero

b. zero Joules

c. < 0

d.> 0 Joules

e. none of these

12. When the high temperature of a Carnot cycle is set to be lower than the low temperature and the first step is reversible isothermal compression, work associated is

a. 0 Joules

b. <0 Joules

c. >0 Joules

d. 0

e. none of these

13. The total heat associated with the Carnot cycle consisting of the isothermal reversible expansion from volume V_1 to V_2, at temperature T_1, adiabatic reversible expansion from volume V_2 to V_3, isothermal reversible compression from volume V_3 to V_4 at temperature T_2 followed by adiabatic reversible compression from volume V_4 to V_1 is

a. $Q_{cycle} = \mathrm{R}\ln(V_2/V_1)\,(T_1 - T_2)$

b. $Q_{cycle} = \mathrm{n\,R}\ln(V_2/V_1)\,(T_1 - T_2)$

c. $Q_{cycle} = -\mathrm{nR}\ln(V_2/V_1)\,(T_1 - T_2)$

d. $Q_{cycle} = -\mathrm{R}\ln(V_2/V_1)\,(T_1 - T_2)$

e. none of these

14.The heat associated with the Carnot cycle (q) is related the corresponding cyclic work (w) as

a. q/w = -1

b. q = 1/w

c. q/w = 1

d. q = w

e. none of these

15. For the Carnot cycle, the following is true

a. change in internal energy is zero

b. only change in enthalpy is zero

c. neither the change in enthalpy nor the change in internal energy is zero

d. only change in the internal energy is zero

e. none of these

16. The definition of change in entropy during a reversible process is

a. the heat appeared or absorbed per 1 K

b. the heat appeared per 1 K

c. neither the heat appeared nor absorbed per 1 K

d. the heat appeared per 1 K

e. none of these

17. The efficiency (ϵ) of a Carnot cycle operating between a high temperature reservoir at T_1 and low temperature sink at T_2 is

a. $\epsilon = 1 + (T_{low}/T_{high})$

b. $\epsilon = 1 - (T_{low}/T_{high})$

c. $\epsilon = 1 - (T_{high}/T_{low})$

d. $\epsilon = 1 - (T_{low} + T_{high})$

e. none of these

18. When heat withdrawn at high temperature is q_1 and heat released at the lower temperature is q_2, the efficiency of the Carnot cycle is

a. $\epsilon = (\,1 + \mathrm{q}_2\,/q_1)$

b. $\epsilon = (1 - q_1 / q_2)$

c. $\epsilon = (1 - q_2 / q_1)$

d. $\epsilon = (1 - q_2 / T_2)$

e. none of these

19. Plot of lower temperature of the Carnot cycle on the x-axis vs efficiency of the cycle on the y-axis is

a. linear and has positive slope

b. linear and has negative slope

c. exponential growth curve

d. exponential decay curve

e. none of these

20. The plot of internal energy vs volume for the Carnot cycle is a

a. rectangle or a square

b. parallelogram

c. circle

d. line

e. none of these

13.13 Self Tests Key

1. c, 2.e, 3. b, 4. c, 5. c, 6. d, 7. d, 8. d, 9. c, 10. a, 11. b, 12. c, 13. b, 14. a, 15. a, 16. a, 17. b, 18. c, 19. b, 20. b.

13.14 Problems

1. Calculate the initial pressure, final pressure, w, q, ΔU, and ΔS for the isothermal reversible expansion of 1 mol of gas from 1 to 5 L, at 300 K. (Ans. 24.6 atm, 4.9 tm, -4.01 kJ, 4.01 kJ, 0 J, 13.38 J/K)
2. Calculate the work done in an adiabatic reversible expansion of 5 mol of gas of heat capacity at constant volume of 1 kJ/K from an initial temperature of 400 K to a final temperature of 300 K. (Ans. 100 kJ)
3. Calculate the work done in a reversible cycle consisting of isothermal expansion of 1 mole of a gas at 500 K from 1 L to 2 L, adiabatic expansion from 500 to 400 K, followed by an isothermal compression at 400 K with a decrease in volume, and then adiabatic compression to the initial state. (Ans. 576 J)
4. Calculate the cyclic work associated with a Carnot cycle when 1 mol of an ideal gas expands from 2 to 3 L at constant temperature 500 K, followed by adiabatic expansion, then isothermal compression from 5 to 3 L at a constant temperature of 300 K followed by adiabatic compression to the initial state. (Ans. -674 J)
5. What is the efficiency of the Carnot engine if it produces 500 J of work during the isothermal expansion and rejects -100 J of heat during the isothermal compression? (Ans. 0.8)
6. What is the efficiency of a Carnot engine working between the two heat reservoirs of high temperature of 1000 K and low temperature of 300 K? (Ans. 0.7)
7. What would be the efficiency of the Carnot engine if the two isothermal steps are carried out at exactly the same temperature? (Ans. 0)
8. If a Carnot engine works with a low temperature reservoir at 300 K, expands the gas in the isothermal step from 3 L to 5 L, how to maximize the efficiency the Carnot engine? (Ans. Set high temperature to infinity).
9. If a Carnot cycle works between the temperatures of 500 K and 300 K, while using 1 mol of an ideal gas to expand from 5 L to 10 L in the isothermal step, and from 10 L to 15 L in the adiabatic step, calculate the efficiency, w_{cycle}, q_{cycle}, ΔU, ΔH and ΔS. (Ans.0.4, -1.1 kJ, 1.1 kJ, 0 J/K)

10. What is the efficiency of the Carnot cycle when the initial and final volumes of the isothermal expansion are one and the same? (Ans. 0)

Chapter 14. Properties of Entropy

After completing this, you will be able to:

- Apply Clausius inequality to natural processes and predict the natural direction of a process.
- Recognize dependence of entropy on pressure, volume, and temperature has been discussed.
- Define the standard entropy of an ideal gas and its dependence on p, V, and T.
- State the third law of thermodynamics was stated and calculate the absolute entropies of substances at room temperature.

Goals

- Analyze Clausius inequality and apply it to real processes.
- Rationalize why time can't be reversed, according to thermodynamics.
- Synthesize expressions for entropy dependence on pressure, V, T, and mole numbers.
- Define the standard entropy of ideal gas.
- State and apply the third law of thermodynamics to calculate the entropies of substances.
- Investigate the molecular descriptions of properties of entropy.

14.1 Why study this?

Entropy is important to establish if a given process moves forward spontaneously or if the reverse process is spontaneous. The magnitude of this quantity, however, depends on the four major thermodynamic variables, n, p, V, and T. Using these relations, in turn, a given process can be tuned to become spontaneous under a specific set of p, V, and T or manipulate the reverse process to become spontaneous. Thus, controlling the spontaneous direction of a processes is an important technological achievement necessary for our culture to thrive. Thus, any insight gained at the practical level to control these processes is vital. For example, chemists want the reactions to occur upon mixing the reactants under specific sets of p, V, T, and concentration or other conditions. These conditions should be such that the reaction occurs spontaneously so that desired product can be maximized.

14.2 Clausius Inequality

The above proof for entropy led us a very interesting observation and this is elaborated below, and the section is divided into two parts for convenience. The first part recognizes the properties of entropy and how it is related to changes during an irreversible process. The second part deals with entropy changes that are occurring in the universe.

14.2.1 Entropy of irreversible processes

Consider any irreversible process. It has the initial state 1 (p_1, V_1, T_1) and final state 2 (p_2, V_2, T_2), connected by an irreversible path, the long blue arrow (Figure 14.1). We design a reversible path from state 2 to state (red curve), which can be purely theoretical and need not be practical, but this will become clear soon.

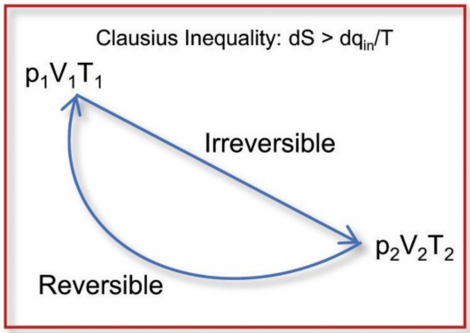

Figure 14.1 Clausius inequality with any irreversible path (straight arrow) from state 1 to state 2. The curved arrow is the reversible path connecting the state 2 back to state 1.

We use the deduction from the previous section for any irreversible cycle and write the following relation for the irreversible cycle shown in Figure 14.1. Even though the back process is reversible the cycle is not.

$$\int_{cycle}\frac{dQ}{T} < 0$$

We divide this integral into two terms, one for step 1 (irreversible) and another for step 2 (reversible), as following.

$$\int_{1}^{2}\frac{dQ_{irreversible}}{T} + \int_{2}^{1}\frac{dQ_{reversible}}{T} < 0$$

We use the definition of entropy and write the second integral for the reversible step.

$$\int_{1}^{2}\frac{dQ_{irreversible}}{T} + \int_{2}^{1}dS < 0$$

Flip the sign of the second integral, exchange the limits, so that both integrals have the same initial and final states.

$$\int_{1}^{2}\frac{dQ_{irreversible}}{T} - \int_{1}^{2}dS < 0$$

For an infinitesimal step of this kind, irreversible forward step and a reversible reverse step, we can write the following in equality where we take the dS term to the other side, leaving the integrals behind.

$$dS > \frac{dQ_{irreversible}}{T}$$

What we have now is a reversible path and an irreversible path, both connecting the same initial and final states, and entropy change dS for the step is greater than $dQ_{irreversible}/T$. Now, a clever argument is placed, described below.

Consider a true isolated system, the Universe which we discussed earlier. Since the universe contains both the system and the surroundings, $dQ_{irreversible}$ must be zero. Heat can neither leave or enter the isolated system because the surroundings are already included in our system.

$$dQ_{irreversible} = 0, isolated\ system$$

From the inequality and the above expression, we conclude that, for any process occurring spontaneously, in an isolated system, the entropy change must be positive!

$$dS > 0, \qquad isolated\ system$$

This is a very powerful argument and states that all irreversible process or spontaneous process or natural processes occurring in the universe are accompanied by an increase in entropy. This is powerful because it generalizes to all irreversible processes happening anywhere in the universe.

This is the partial answer for our quest, and it is partial only because we need to measure entropy change of the system and that of the system, only then we will get the entropy change of the universe due to our process. This is correct, but bit cumbersome as discussed further, below.

14.2.2 Entropy is times arrow

$$dS > 0, \qquad isolated\ system$$

The above result is powerful because it can predict if a given chemical reaction can occur spontaneously, just by mixing the reactants for example, or not. Remember we wanted to know if a chemical reaction would take place by itself. Now we claim, yes, the chemical reaction will occur if "dS" is greater than zero for that chemical reaction, when measured with an isolated system or that of the universe. Considering the universe, for us, means we calculate the change in the entropy of the system, and calculate the entropy change in the surrounding and sum them together. It this is greater than zero, then we have a spontaneous reaction taking place. Because of the spontaneous processes happening in our universe, the entropy of the universe is increasing as a function of time. Thus, it is said that entropy is times arrow. Thus, you may find bumper stickers of ‘Entropy is not what it used to be’.

Example 14.1

Define entropy changes when fuel is burned in the gasoline engine to propel your car.

We define the cylinder, with filled with fuel before the spark plug ignites it, as the system, and the boundary of the gas as the surroundings. We choose this as an open system so that we can add the fuel, spark the plug and allow the work to appear at the boundary of the system and move the car. As we heat the gases by igniting and burning the fuel with oxygen in the cylinder, entropy of the system is increasing due to the increase in the temperature, pressure and also the increase in the mole numbers. For example, gasoline is long chain hydrocarbon and when it is burned in air to produce carbon dioxide and water, the mole numbers are increasing as well.

Increase in the temperature and the mole numbers during the combustion process also increases the pressure of the gases before the piston moves up. We learned that increase in pressure decreases the entropy and the net change in entropy, thus far, depends on the magnitudes of the entropy increases due to the temperature, mole numbers and the pressure.

Volume of the gases is another player that can contribute to entropy. As the gases expand in the cylinder, push the piston out, they occupy more space and hence, there is an increase in the entropy of the system due to volume expansion. Thus, the net change in entropy depends on the exact contributions of the above variables to entropy.

We also need to consider the surroundings to account for the entropy changes of the universe. This is because, the total entropy change which includes that of the system and the surroundings is a predictor for the natural direction of the combustion process. As the piston moves up and turns the crank shaft of the motor, the wheels turn, and the car moves. This process in the surroundings is performing work and increasing its entropy. As the cylinders are firing and recharging with fresh air and fuel, the combustion gases are released into the atmosphere, and this also increases the entropy of the surroundings.

In addition to the above changes to entropy to the surroundings, various motions of the car parts convert some of the mechanical energy into heat, raising the entropy of the surroundings. As the car moves, it might crush the pavement, distort the tires and increase the entropy way as well. Thus, a variety of mechanisms are involved in the process, and include both the system as well as the surroundings that contribute to the total entropy change of the universe. But we can be certain that the total entropy must be >0, as the burning of the fuel and the motion of the car is a spontaneous process or a natural process.

We now have a good predictor to say whether the chemical reaction or a physical process would occur spontaneously, if we can measure entropy changes in both the system, surroundings, and the sum is greater than zero. Often, this kind of analysis is problematic because the analysis includes surroundings and gets more complicated. So, yes, entropy is a good predictor to predict whether that a chemical reaction or a physical process would occur spontaneously, but we need to include both the system and the surroundings in our analysis. In a later chapter, we will address this issue, but for now, we are good to go and examine the properties of the new state function, entropy.

14.3 Entropy Dependence on p, V, and T

In an independent vein, entropy in its own right is a very important property of the system. Therefore, we are very much interested in figuring out the temperature, pressure, volume dependence of entropy. We use ideal gas as our model to examine these dependencies, because this is a bit more convenient than using real gases for the following derivations.

14.3.1 Entropy Dependence on V and T

We begin our discussions with the volume and temperature dependence of entropy. These are very important variables in many of our experiments because keeping the pressure is of convenience. Many of our derivations will start with the second law of thermodynamics, add the first law, and make substitutions as needed, as shown below.

$$\mathrm{d}S = \frac{\mathrm{d}Q_{rev}}{T}$$

We substitute for Q in the above, using the first law of thermodynamics, given as below.

$$\mathrm{dU} = dq + dw$$

$$\mathrm{T\ dS} = \mathrm{d}Q_{rev} = dU + p\,dV$$

This combination of the first and the second laws is powerful, and we could derive many thermodynamic equations from this one equation.

We replace dU in terms of a T-term, using the relation that dU = C_v dT, and write the following.

$$\mathrm{T\ dS} = C_V\,dT + p\,dV$$

Rearranging and using the ideal gas law, we can write the pV term in two steps, as following.

$$\mathrm{dS} = C_V\,(1/T)\,dT + \left(\frac{p}{T}\right)dV$$

$$= C_V\,(1/T)\,dT + (n\,R/V)\,dV$$

The above expression has both the T and V dependencies for an ideal gas, and Cv, n, and R are constants and hence, ready for integration with limits of initial and final states to get the final expression.

$$\Delta\mathrm{S} = C_V\ln(T_2/T_1) + n\,R\ln\left(\frac{V_2}{V_1}\right)$$

In the above, T_1 and T_2 are the temperatures of the initial and final state and V_1 and V_2 are the volumes of the initial and final state volumes, respectively. We conclude from the above relation that entropy an ideal gas increases with temperature, as well as the volume in a logarithmic fashion. This is illustrated in Figure 14.2 (A, B).

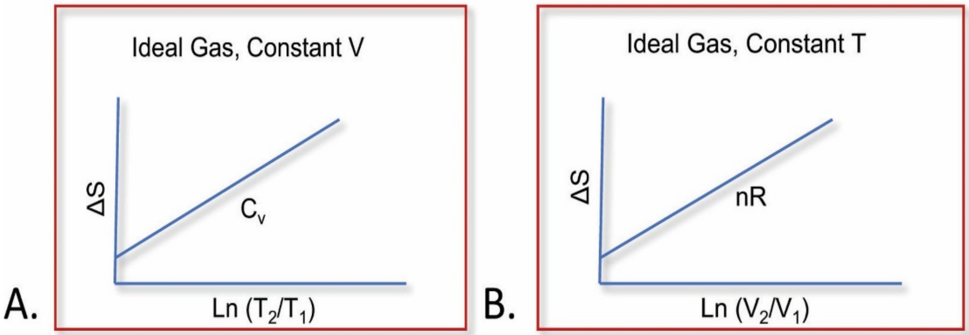

Figure 14.2 Plot of ΔS of ideal gas as the logarithmic function of temperature (A., left, constant volume) and as a function of volume (B., right, constant temperature). The linear plot on the left has a slope of C_v, while the slope of the plot on the right is nR. The intercepts are zero in both plots, because when the volume is constant, or when temperature is constant, the corresponding logarithmic term is zero.

This figure teaches us that entropy increases for an ideal gas as we heat it under constant conditions or when we allow it to expand under isothermal conditions. Thus, we can readily connect our previous discussions with entropy, using the above expression.

Example 14.2
Calculate the entropy change when a gas expands in an automobile engine from an initial volume of 200 cc to a final volume of 500 cc, at an initial pressure of 12 atm and temperature of 800 K. Assume expansion is isothermal, and ideal behavior for the gas.

ΔS = nR ln (V_2/V_1) = n R ln (500/200), at constant T, but we need the value of n.

Assuming ideal gas behavior, nR = pV/T = [12 atm * 200 cc (1 L/1000 cc) / 800 K].

ΔS = nR ln (V_2/V_1) = [12 atm * 200 cc (1 L/1000 cc) / 800 K] * ln (500/200) = 0.00275 L atm/K

Converting L atm into joules by multiplying with 101.325 J/L atm, we get ΔS = 0.278 J/K. The small increase in entropy is due to the assumption of isothermal expansion. Increase in entropy makes sense, as the volume is increasing at constant temperature.

Example 14.3

Calculate the entropy change when a gas expands from an initial volume of 200 cc to a final volume of 500 cc, at an initial pressure of 12 atm and temperature of 800 K. Assume expansion is adiabatic and ideal behavior for the gas.

$$\Delta S = C_V \ln(T_2/T_1) + n\,R\ln\left(\frac{V_2}{V_1}\right)$$

But we need the values of nR, C_v, C_p/C_v, and the final temperature.

Assuming ideal gas behavior, nR = pV/T = [12 atm * 200 cc (1 L/1000 cc) / 800 K] = 0.0366 L atm/K

C_v = 1.5 nR = 0.055 L atm/K

$\gamma = C_p/C_v = 2.5/1.5$

$$\frac{T_2}{T_1} = \frac{V_1^{\gamma}}{V_2^{\gamma}} = \frac{0.2^{\frac{2.5}{1.5}}L}{0.5^{\frac{2.5}{1.5}}L} = 0.217$$

ΔS = 0.055 L atm/K * ln(0.217) + 0.0366 L atm/K ln(0.5/0.2) = -0.0502 L atm/K

Converting L atm into joules by multiplying with 101.325 J/L atm, we get ΔS = -5.09 J/K. The decrease in entropy is due to the adiabatic expansion as the temperature is dropping and its contribution overpowers entropy increase due to volume increase.

14.3.2 Entropy as a function of p and T

Here, we will examine how the entropy of an ideal gas changes as we change the pressure and temperature. Even though keeping p constant is convenient, we need this variable in some of the high-pressure experiments or in studying many natural processes. Thus, pressure is a key variable for us.

We take advantage of the fact that we have derived the temperature-volume relationship and make substitutions using the ideal gas law. We start with the following equation, we just derived.

$$\Delta S = C_V \ln(T_2/T_1) + n\,R\ln(V_2/V_1)$$

All we must do is replace the volume terms with the corresponding pressure terms and we will have the desired equation, and we proceed as follows. For an ideal gas, we recognize that the ratio of volumes is equal to the ratios of the pressure to temperature or as following.

$$V_2/V_1 = T_2\,p_1/T_1\,p_2$$

Substituting the above relation in the equation for ΔS, we get the following.

$$\Delta S = C_V \ln(T_2/T_1) + n\,R\,\ln(T_2 p_1/T_1\,p_2)$$

$$\Delta S = C_V \ln(T_2/T_1) + n\,R\,[\ln(T_2/T_1) + \ln(p_1/p_2)]$$

In the next step, we take advantage of the presence of the C_v and nR terms and use the relation $C_p - C_v$ = nR and rearrange to simplify the temperature terms further.

$$\Delta S = C_V \ln(T_2/T_1) + (C_p - C_V)\,[\ln(T_2/T_1) + \ln(p_1/p_2)]$$

Expanding the parenthesis, we get all the five terms and try to cancel some of them, as shown.

$$\Delta S = C_V \ln(T_2/T_1) + C_p\,\ln(T_2/T_1) + C_p\,\ln(p_1/p_2) - C_V \ln(T_2/T_1) - C_V\,\ln(p_1/p_2)$$

We recognize that we can cancel the first and the fourth terms, while combining the pressure terms.

$$\Delta S = C_p \ln(T_2/T_1) + \left(C_p - C_V\right)\ln(p_1/p_2)$$

We now take advantage of the relation $C_p - C_v$ = nR and simplify further which shows the relation between entropy change, T and p of an ideal as.

$$\Delta S = C_p \ln(T_2/T_1) + n\,R\ln(p_1/p_2)$$

We flip the ratio of pressures to get the alternate expression, as following.

$$\Delta S = C_p \ln(T_2/T_1) - n\,R\,\ln\,(p_2/p_1)$$

The above equation teaches us that a plot of ΔS as a function of pressure, at constant T (isothermal process), we will get an exponential decay. Thus, the entropy change will fall off with increase in pressure, exponentially (Figure 14.3). This contrasts with increase of entropy with volume, we witnessed above. If we plot the log of the pressure, we will get a linear plot with a slope of – nR.

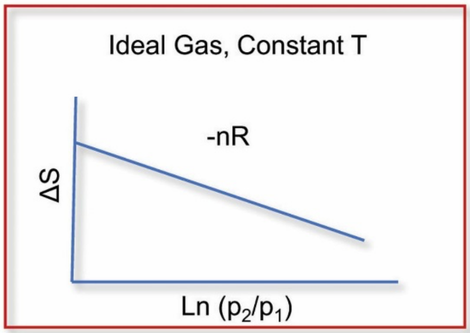

Figure 14.3 Plot of ΔS of ideal gas as the logarithmic function of pressure (left, constant T) and as a function of ln(p) (right, constant T). The exponential plot on the left shows how rapidly entropy falls off with increase in pressure. The linear plot on the right has a slope of nR. The intercept is zero in the linear plot, because when the T is constant, the corresponding logarithmic term is zero.

As we increase the temperature at constant T or V, the entropy of the system increases for an ideal gas. In contrast, entropy decreases with increase in pressure. Thus, we have examined how the entropy changes are influenced by the T, p, and V changes for an ideal gas.

In summary, entropy increases logarithmically with temperature and volume of an ideal gas, while it decreases logarithmically with increase in pressure. The physical significances of these relations will be examined later but first, we will examine another important graph.

Example 14.4
Calculate the entropy change when a gas expands in an automobile engine from an initial pressure of 12 atm, 200 cc and 900 K to a final pressure of 2 atm and 300 K, adiabatically and irreversibly. Assume ideal behavior for the gases. Explain your result.

$$\Delta S = C_p \ln\left(\frac{T_2}{T_1}\right) - n\,R\,\ln\left(\frac{p_2}{p_1}\right)$$

We construct a reversible path to use the above equation and we also need C_p and nR for the calculations.

For an ideal gas, C_p = 2.5 nR, nR = pV/T = 12 atm 200 cc (1 L/1000 cc) /900 K = 0.0027

ΔS = 2.5*0.0027* ln(300/900) – 0.0027 ln(2/12) = -0.0025 (L atm/K)*(103.25 J)/(1 L atm) = - 0.258 J/K

The answer makes sense, as the expansion lowers entropy due to the decrease in temperature and entropy increase is due to decrease in pressure as well as increase in volume. However, the temperature factor in the above equation is multiplied by Cp, which is 3.5 nR, while the pressure term is multiplied by nR. Thus, temperature contributes more than pressure, in that way, and the answer makes sense.

14.3.3 Entropy as a function of T in an isobaric process

We can impose the constant pressure conditions in the equation we just obtained and examine the temperature dependence of entropy for an isobaric process. We get the following expression and a plot of entropy vs logarithm of temperature for an ideal gas (Figure 14.4) shows a line with slope equal to C_p.

$$\Delta S = C_p \int_1^2 \frac{1}{T}\,dT$$

$$\Delta S = C_p \ln\left(\frac{T_2}{T_1}\right)$$

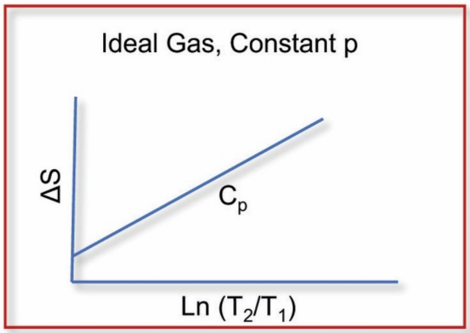

Figure 14.4 Plot of ΔS as the logarithmic function of temperature at constant pressure, for an ideal gas. Entropy increases with temperature in a logarithmic manner with a slope equal to C_p, while the slope of the corresponding plot at constant volume conditions will be C_v.

Thus, entropy increases with T for an ideal gas during an isobaric process and the slope of the plot is C_p. We recognize that slope of a similar plot for an isochoric process has a slope of C_v. The entropy changes can be understood readily in terms of energy and space distributions of molecules, and this is the focus of the next chapter. Now, however, we will examine other important properties of entropy.

Example 14.5

A gas sample was heated under isobaric conditions from 300 K through 200 K. What is the change in its entropy?

$$\Delta S = C_p \ln\left(\frac{T_2}{T_1}\right)$$

We need C_p and number of moles to do the calculations. Since the value is not given and nature of the gas not specified, we assume that it is an ideal gas of 1 mole, and use C_p= 2.5 R.

$$\Delta S = 2.5 * 8.314 \frac{J}{mol\ K} \ln\left(\frac{500}{300}\right) = 10.6 \frac{J}{mol\ K}$$

The answer makes sense because increase in temperature increases entropy of the gas.

14.4 Standard State of Entropy and Coefficients of Expansion and Compression

14.4.1 Standard entropy of an ideal gas

Defining the standard state helps in experimental measurements but we will define this for an ideal gas. The standard state for entropy of an ideal gas is defined as entropy at one atmosphere at some reference temperature of our choice (1 atm, constant T). Then, we can write ΔS with reference to the standard state, as follows.

$$\Delta S = S_2 - S^\circ = -n\,R \ln{(p_2/p_1)}$$

$$\Delta S = S_2 - S^\circ = -n\,R \ln{(p_2\,atm/1\,atm)}$$

A plot of S_2-S°, using the standard state, we see that the entropy increases with pressure, as we saw before, except that the initial pressure is 1 atm (Figure 14.5).

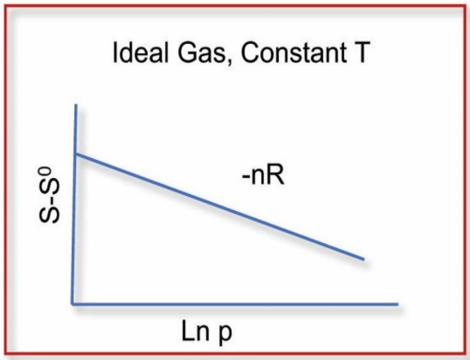

Figure 14.5 Plot of S_2-S˚ for the ideal gas as logarithmic function of pressure with a slope of - nR.

Example 14.6

The standard molar entropy at 300 K for helium is 126.2 J/K mol, what is its molar entropy at 400 atm?

$$S_2 = S^\circ - n\,R\ln\left(p_2\,atm/1\,atm\right)$$

$$S_2 = 126.2\frac{J}{K\,mol} - 1 * 8.314\frac{J}{K\,mol}\ln\left(\frac{400\,atm}{1\,atm}\right) = 76.39\,J/Kmol$$

The answer makes sense because increase in pressure decreases entropy, and entropy at higher pressure is lower than at 1 atm.

14.4.2 Coefficients of thermal expansion and compressibility

Learning to write the exact differentials and using them for derivations of thermodynamic functions is an important exercise. This approach provides additional insight into the nature of entropy, and we obtain additional relations between the quantities we already know, as following.

Since entropy depends on temperature and pressure for the ideal gas, we would expect S to depend on the coefficients of expansion and compressibility as well. Using the exact differentials, and a length derivation, we can connect these important experimental parameters with entropy.

Since S is a state function, we can write the exact differential dS as following.

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

If we apply constant temperature conditions, as part of our investigation, dT = 0, and we have only the volume terms.

$$dS = \left(\frac{\partial S}{\partial V}\right)_T dV$$

We recall the combination of the first and second laws and then construct a parallel equation for dS at constant T conditions. The need for this, becomes clear soon.

$$T\,dS = dU + p\,dV = C_V\,dT + [(\partial U/\partial V)_T + p]\,dV$$

Setting dT = 0, and rearranging the T term, we get the desired equation.

$$dS = \frac{1}{T}\left[p + \left(\frac{\partial U}{\partial V}\right)_T\right] dV$$

We compare the equation for dS from above with the one obtained earlier, and each term on the right of the dS relation must be equal in both equations. Equating them, we get the following.

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T}\left[p + \left(\frac{\partial U}{\partial V}\right)_T\right]$$

Now, we set dV = 0 in the equation obtained by combining the first and second laws to get the following.

$$T\,dS = C_V\,dT + [(\partial U/\partial V)_T + p]\,dV, \qquad set\ \ dV = 0$$

$$T\,dS = C_V\,dT$$

From the above, we write the other important differential function for S as following.

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{1}{T}\,C_V$$

These equations by themselves did not give us what we are looking for but a second derivate may be useful to get the coefficients of expansion and compression.

The second derivative of the $\left(\frac{\partial S}{\partial T}\right)_V$ with respect to V, gives the following expressions.

$$\frac{d}{dV}\left(\frac{\partial S}{\partial T}\right)_V = \frac{\partial^2 S}{\partial V\,\partial T} = \frac{d}{dV}\left(\frac{1}{T}\,C_V\right) = \frac{1}{T}\,\frac{\partial^2 U}{\partial V\,\partial T}$$

The second derivative of the $\left(\frac{\partial S}{\partial V}\right)_T$ with respect to T gives the following expression.

$$\frac{d}{dT}\left(\frac{\partial S}{\partial V}\right)_T = \frac{\partial^2 S}{\partial V\,\partial T} = \frac{d}{dT}\,\frac{1}{T}\left[p + \left(\frac{\partial U}{\partial V}\right)_T\right] = \frac{1}{T}\left[\left(\frac{\partial p}{\partial T}\right)_V + \frac{\partial^2 U}{\partial V\,\partial T}\right] - \frac{1}{T^2}\left[p + \left(\frac{\partial U}{\partial V}\right)_T\right]$$

Comparing the two double derivatives from above, which should be exactly equal, we get the following new relation.

$$\frac{1}{T}\frac{\partial^2 U}{\partial V\,\partial T} = \frac{1}{T}\left[\left(\frac{\partial p}{\partial T}\right)_V + \frac{\partial^2 U}{\partial V\,\partial T}\right] - \frac{1}{T^2}\left[p + \left(\frac{\partial U}{\partial V}\right)_T\right]$$

Cancelling the two second derivative terms of U, on both sides of the above equation, we get the following.

$$0 = \frac{1}{T}\left(\frac{\partial p}{\partial T}\right)_V - \frac{1}{T^2}\left[p + \left(\frac{\partial U}{\partial V}\right)_T\right]$$

We have already shown that $\left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T}\left[p + \left(\frac{\partial U}{\partial V}\right)_T\right]$, and so, we substitute left side of this for the second term in the above equation and rearrange it to obtain the relation we seek.

$$0 = \frac{1}{T}\left(\frac{\partial p}{\partial T}\right)_V - \frac{1}{T}\left(\frac{\partial S}{\partial V}\right)_T$$

Since, the subtraction of these two terms is zero, we can safely write the following expression.

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$$

But, we have the following relation which we arrived much earlier.

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{\alpha}{\kappa}$$

Thus, we can write the following two expressions.

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{\alpha}{\kappa}$$

$$dS = \frac{\alpha}{\kappa}\,dV$$

By integrating this expression with limits of initial (1) and final (2) states, we get the following relation that we are looking for.

$$\Delta S = \frac{\alpha}{\kappa}\,(V_2 - V_1)$$

Plot of S vs V should give a straight line with a slope equal to α/κ and this is illustrated in Figure 14.6. Compare this with the plot of S vs V, obtained earlier.

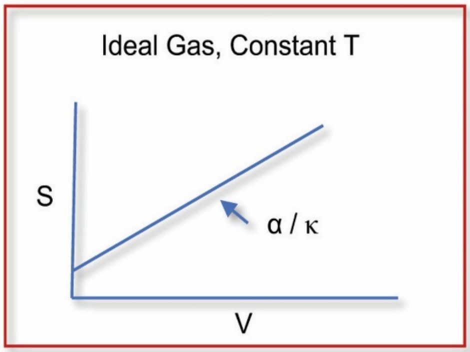

Figure 14.6 Plot of S vs V for the ideal gas with a positive slope of α/κ. Entropy change per unit volume is a constant.

Thus, S, V, p, and T are related to the heat capacities and the coefficients of thermal expansion and compressibility. Entropy changes can be predicted as a function of pressure, temperature, and volume.

Example 14.7

The change in entropy when a liquid of coefficient of thermal expansion of $2.07\text{X}10^{-4}$/K compressed from 2 L to 1.999 L was 10 J/K at constant temperature. What is its compressibility factor?

$$\Delta S = \frac{\alpha}{\kappa}(V_2 - V_1)$$

We need the compressibility factor which is given as

$$\kappa = \frac{\alpha}{\Delta S}(V_2 - V_1) = \frac{0.000207\ K}{K*(10)\ J} * \frac{101.325\ J}{1\ L\ atm}(2\ L - 1.999\ L) = 2.09 * 10^{-6}/atm$$

This value makes sense, as it is very small on the order of known values for most liquids and also positive with correct units.

14.5 Entropies of Phase Transitions

One of the major experimental measures of entropy involves phase transitions, because these are reversible transformations. Thus, we can measure the entropy changes for these transitions easily, and these values are of high importance for calculating the absolute entropies of substances using the third law of thermodynamics. Phase transitions are carried out usually, under isobaric, isothermal, and reversible conditions. They are isothermal because the temperature does not change during the transition until one of the phases is consumed completely.

These transitions are isobaric because, we usually carry these measurements at 1 atm, open to the atmosphere, and hence, the pressure is kept constant automatically at this value. The equilibrium between the two phases ensures that the transition is reversible. We discussed ice-water equilibrium, when a small amount of the substance is transformed from phase 1 to phase 2 in the forward direction, then a small amount of phase 2 is converted to phase one during the reverse direction, keeping the temperature constant (Figure 14.7 A, B).

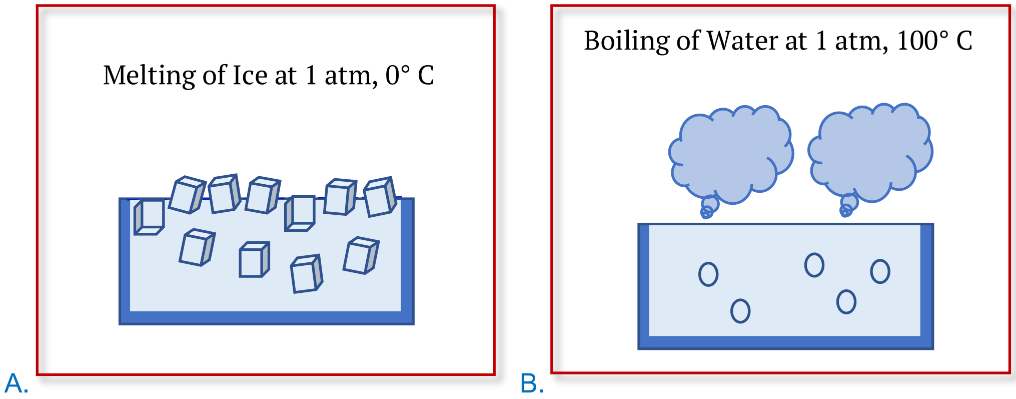
Melting of Ice at 1 atm, 0° C
A.
Boiling of Water at 1 atm, 100° C
B.

Figure 14.7 A. Phase transitions of ice/water and B. water/steam, at 1 atm and the corresponding transition temperatures.

From the definition of entropy of any process from state 1 to state 2, we write the following expression.

$$\Delta S = \int_1^2 \frac{dQ_{reversible}}{T}$$

Since phase transition is an isothermal process, we write the above by pulling the temperature term out of the integral.

$$\Delta S = \frac{1}{T}\int_1^2 dQ_{reversible}$$

Using the first law, we write the heat term in terms of internal energy, pressure, and volume, as following. Note that we are assuming that all work is pV work, because this is an isobaric process, and the external pressure is kept equal to the pressure of the system.

$$\Delta S = \frac{1}{T}\int_1^2 (dU + p\, dV)$$

We recognize that the operand is simply dH, under isobaric conditions, and replace with it.

$$\Delta S = \frac{1}{T}\int_1^2 dH$$

Upon integration of the expression between the two limits, we get the final expression, relating the entropy change with the enthalpy change and the temperature T, where the transition takes place.

$$\Delta S = \frac{\Delta H}{T}$$

The signs on ΔH and ΔS depend on the direction of the process. For example, if ΔH is positive as in the case of ice to water phase transition, then ΔS and ΔH are positive and temperature in kelvin is always positive.

$$\Delta H > 0 \; then \; \Delta S > 0, boiling$$

$$\Delta H < 0 \; then \; \Delta S < 0, snowing$$

However, ΔH is negative and ΔS is also negative for the reverse transition, phase transitions are carried out under isobaric and isothermal conditions, or else the above equation is no longer applicable. When the pressure is 1 atm then these are normal boiling points or normal melting points or normal freezing points etc., When we convert ice to water or most solids to their corresponding liquids, entropy increases. This is essentially because the molecules in the liquid have a higher degree of freedom to roam around, and this freedom increases their entropy.

Example 14.8

The enthalpy of freezing of liquid water is -6.0 kJ/mol at 0 ˚C and 1 atm. What is ΔS for this transformation?

$$\Delta S = \frac{\Delta H}{T} = \frac{-6.0\ kJ/mol}{273.15\ K} = -21.97\ J/Kmol$$

The answer makes sense because the entropy decreases on freezing, it has the right units, and the arithmetical value is correct.

14.6 The 3rd Law of Thermodynamics

The third law of thermodynamics defines the entropy of a perfectly crystalline pure substance at 0 K, and this is important for calculating the absolute entropies of substances at room temperature and 1 atm, pressure. Thus, the third law is important for entropy calculations of pure substances which in turn are useful to calculate entropies of reactions from the corresponding elemental states and the stoichiometry of the chemical reaction at hand.

Third Law states that entropy of a perfectly crystalline, pure substance at 0 K is zero. This is a hypothetical state. Because getting to 0 K itself is not possible. Secondly, we need a pure and perfectly crystalline substance, and even a minute impurity will violate the requirement. But for all practical purposes, we can practice the third law of thermodynamics without difficulty, as following. This is the lowest entropic state a substance can have. For these reasons, we call these as the absolute entropy values.

Starting from this state defined by the third law at 0 K, we can compute the absolute entropy of any substance at room temperature. We heat the sample from 0 K up to room temperature, for example, and measure the entropy changes along the way, as illustrated by steps 1 through 5.

Solid at 0 K → Solid at T_m + ΔS_1 1

Solid at T_m → Liquid at T_m + ΔS_2 2

Liquid at T_m → Liquid at T_b + ΔS_3 3

Liquid at T_b → Vapor at T_b + ΔS_4 4

Vapor at T_b → Vapor at T + ΔS_5 5

We developed the pertinent equations to account for entropy changes due to increase in temperature, and if there are phase changes such as melting or boiling along the way from 0 K to room temperature, we add these corresponding entropy changes to obtain the entropy of the substance, as shown below.

$$\Delta S = C_{p,solid}\int_0^{T_m}\frac{1}{T}\,dT + \frac{\Delta H_m}{T_m} + C_{p,liquid}\int_{T_m}^{T_b}\frac{1}{T}\,dT + \frac{\Delta H_b}{T_b} + C_{p,gas}\int_{T_b}^{T}\frac{1}{T}\,dT$$

The first integral accounts for entropy change (ΔS_1) for heating the sample from 0 K to its melting point (T_m), having a heat capacity of $C_{p,\,solid}$. The second term accounts for the entropy change (ΔS_2) due to the phase transition of solid to liquid phase having enthalpy of melting (ΔH_m) at its melting point (T_m). The third term accounts for the heating of the liquid from its melting point to its boiling point (T_b) with its heat capacity ($C_{p,\,liquid}$). The fourth term accounts for the entropy change (ΔS_4) for the phase transition from the liquid to the gas at its boiling point (T_b) and heat of evaporation (ΔH_b), and the last term accounts for the heating of the vapor from the boiling point to room temperature with its corresponding heat capacity ($C_{p,\,gas}$). We write the absolute entropies of substances or the third law entropies by summing the above five values.

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4 + \Delta S_5$$

In summary, the third law sets the lowest entropy value for a pure, crystalline substance at 0 K to be zero, and allows us to calculate the absolute entropies of substances in a systematic manner. These entropies for numerous substances at 1 atm and 300 K are already established. However, recent work shows that neither the third law nor quantum chemistry is necessary to assign entropy of a pure substance at 0 K.[27]

Table 14.1 Standard entropies of a few substances at 25 ˚C, 1 atm.

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[27] A. M. Steane, On determining absolute entropy without quantum theory or the third law of thermodynamics, *New J. Phys.,* Volume 8, pp 043022, year **2016**

Substance	*Formula*	*ΔS° (J/Kmol)*
Diamond	C	2.38
Graphite	C	5.74
Ammonia	NH_3	192.5
Methanol	CH_3OH	126.8
Ethanol	C_2H_5OH	160.7
Water	H_2O	69.9
Carbon dioxide	CO_2	213.7
Methane	CH_4	186.3
Oxygen	O_2	205.0
Hydrogen	H_2	130.7

Example 14.9

A sample of solid hydrogen was heated to gas at 1 atm from 0 K to room temperature, calculate its molar absolute entropy. [$C_{p,solid}$(J/mol K):49.2; $C_{p,liquid}$(J/mol K):10; $C_{p,gas}$(J/mol K):14.3; $T_{melting}$/˚C:-259; $T_{boiling}$/˚C:-252.9; ΔH_{fusion}(kJ/mol):0.05868; $\Delta H_{boiling}$(kJ/mol):0.449]

$$\Delta S = C_{p,solid}\int \frac{1}{T}dT + \text{constant} + \frac{\Delta H_m}{T_m} + C_{p,liquid}\int_{T_m}^{T_b}\frac{1}{T}\,dT + \frac{\Delta H_b}{T_b} + C_{p,gas}\int_{T_b}^{T}\frac{1}{T}\,dT$$

Substitution of the above parameters into the equation, setting the constant to '0' by the third law, we get the following.

$$\Delta S = 49.2\frac{J}{mol\ K}ln\left(\frac{14.1}{1}\right) + 58.68\frac{J}{14.1\ mol\ K} + 20\frac{J}{mol\ K}\ln\left(\frac{20.2\ K}{14.1\ K}\right) + 449.36\frac{J}{20.2\ mol\ K} + 28.6\frac{J}{mol\ K}\ln\left(\frac{273.15\ K}{20.2\ K}\right) = 238.27\frac{J}{mol\ K}$$

The answer makes sense as it is positive, has right units and nearly the same as reported value. Some deviations are to be expected from the measured values as the heat capacities themselves are functions of temperature, and these have not been accounted for, here. Also, near 0 K, the above integral is not valid, and numerical estimates are made from plots of C_p and temperature.

14.7 Molecular interpretation

The molecular description of entropy is quite simple, indeed. It is considered as the degree of disorder (discussed at length in the next chapter). Then, we can readily envision how it decreases with pressure, but increases with volume and temperature. For example, increasing the volume increases the degree of randomness as the gas particles attempt to occupy all the space available to them. But, when we increase pressure by compressing at constant temperature, the volume decreases, and hence, from the above picture, the degree of disorder decreases. By increasing the temperature at constant volume, or constant pressure, the randomness increases because the particles have higher kinetic energies and traveling faster and faster. Thus, the influence of p, V, and T on entropy can be readily understood.

Specific heat and entropy are related. Increasing the specific heat increases the entropy. Because you need energy to raise the temperature by a degree and this contributes to a rise in the kinetic energy of the gas particles, increasing its randomness and hence, its entropy. The greater the heat capacity, the greater the entropy of the substance.

The third law of thermodynamics utilizes the high degree of order expected when the substance is pure, perfectly crystalline and at 0 K. When the substance is pure, there are no impurities in the sample, all particles are exactly chemically and magnetically identical. Thus, pure substances have lower entropy than impure substances. Analogously, the degree of crystallinity also influences the degree of randomness and hence, a perfectly crystalline pure substance does not have disorder and hence, should have lower entropy than less crystalline but pure substance. Last but not the least, the degree of disorder increases with temperature. Since 0 K is the lowest temperature ever attainable, the lowest degree of disorder is possible only at 0 K, and when a substance meets all the above three criteria, we have the lowest entropy state. This value is set to zero, because entropy of the substance can't be any lower than this value, and hence, it must be the zero-entropy state. Thus, the third law allows us to calculate absolute entropies of pure substances at room temperature via systematic entropy measurements.

14.8 Applications in daily Life

A discussed in the previous chapter, entropy increase is associated with all irreversible processes and entropy increase is used in our daily lives for a variety of applications. Think about these.

14.9 New Terms and units

General proof for entropy as a state function, Clausius inequality, ratio of heat capacities, entropy of the universe, absolute entropies, and the third law of thermodynamics. Entropy has the SI units of joules/K, and the corresponding base units of kg m^2 s^{-2} K^{-1}.

14.10 Key points

1. General proof for entropy as a state function was obtained by an elaborate method but the key argument was that heat can't flow spontaneously from a low temperature to high temperature.
2. The above argument is powerful and clearly established entropy as a state function by demonstrating that the cyclic integral of entropy is zero for all cycles.
3. Utilizing the above proof, and constructing an irreversible cycle, the entropy change for an irreversible process is expressed. This is useful for practical applications, but it also indicated that the entropy changes occurring in the universe are positive due to the various natural processes happening there.
4. Clausius inequality clearly demonstrated that the entropy changes of irreversible processes are contributing to the increase in the entropy of the universe. Entropy is not what it used to be, it is increasing and increasing.
5. Entropy increases exponentially with increase in temperature or increase in volume.
6. The rate of change of entropy with volume is a constant, ratio of thermal expansion to compressibility.
7. Entropy decreases exponentially with increase in the pressure.
8. The third law of thermodynamics sates that a pure, perfectly crystalline substance at 0 K has the lowest possible entropy, which can be set to zero.
9. Using the third law, the absolute entropies of substances can be obtained by summing all the entropy changes when the sample is brought from 0 K to room temperature.

14.11 Self Reflection

1. Identify 3 different process in the space of your dorm room that are accompanied by increases in entropy and at least one that is accompanied by a decrease in entropy.
2. Assume that heat can flow spontaneously from low temperature to high temperature and argue what contradictions you may arrive at.
3. Plot S vs T, ΔS vs T, ΔS vs V and ΔS vs p for an ideal gas.
4. Explain why $\Delta S/\Delta V$ is a constant in terms of molecular theory.
5. If entropy of the universe is increasing with time, where is the energy coming from and where is it going?

14.12 Further Reading

1. https://ocw.mit.edu/courses/chemistry/5-60-thermodynamics-kinetics-spring-2008/video-lectures/lecture-8-second-law/
2. https://ocw.mit.edu/courses/chemistry/5-60-thermodynamics-kinetics-spring-2008/video-lectures/lecture-10-entropy-and-irreversibility/

3. https://ocw.mit.edu/courses/aeronautics-and-astronautics/16-01-unified-engineering-i-ii-iii-iv-fall-2005-spring-2006/thermo-propulsion/

14.13 Self Tests

1. We need to recognize entropy and its properties because

   a. it can predict if a given process is spontaneous

   b. it can show that the reverse of a given process is spontaneous

   c. it can predict the internal energy of the system

   d. it can predict the enthalpy of a system and its surroundings

   e. none of these

2. One of the definitions of entropy is

   a. $dT_{reversible}/q$

   b. $dq_{reversible}/T$

   c. dq/T

   d. $dU_{reversible}/T$

   e. none of these

3. The heat of an infinitesimal step of a reversible cycle ($dQ_{reversible}$) and the corresponding temperature (T) are related as

   a. $\int_{cycle} \frac{dU_{rev}}{T} = 0$

   b. $\int_{cycle} \frac{dH}{T} = 0$

   c. $\int_{cycle} \frac{dQ_{rev}}{T} = 0$

   d. $\int_{cycle} \frac{dS_{rev}}{T} = 0$

   e. none of these

4. For the Carnot cycle, the heat (Q) and the corresponding temperature (T) are related as

   a. $\int_{cycle} \frac{dU_{carnot}}{T} = 0$

   b. $\int_{cycle} \frac{dQ_{carnot}}{T} = 0$

   c. $\int_{cycle} \frac{dV_{carnot}}{T} = 0$

   d. $\int_{cycle} \frac{dT_{carnot}}{q} = 0$

   e. none of these

5. For any cycle, reversible or not, the following is true (S, entropy),

   a. $\int_{cycle} dS > 0$

   b. $\int_{cycle} dw = 0$

   c. $\int_{cycle} dq = 0$

   d. $\int_{cycle} dS = 0$

   e. none of these

6. For any irreversible cycle, the heat that appears ($Q_{irreversible}$) and work that appears ($w_{irreversible}$) during a process of the cycle at temperature T, the following is true,

   a. $\int_{cycle} \frac{dw_{reversible}}{T} < 0$

   b. $\int_{cycle} \frac{dQ_{irreversible}}{T} < 0$

   c. $\int_{cycle} \frac{dw_{irreversible}}{T} < 0$

   d. $\int_{cycle} \frac{dQ_{reversible}}{T} < 0$

   e. none of these

7. For any process occurring in an isolated system, Clausius inequality shows

   a. $dS > 1$

   b. $dS < 0$

   c. $dS = 0$

   d. $dS > 0$

   e. none of these

8. A combination of the first and second laws (standard symbols used) is,

   a. $\mathrm{T\,dp} = \mathrm{d}Q_{rev} = dU + p\,dV$

   b. $\mathrm{T\,dS} = \mathrm{d}Q_{reversible} = dU + p\,dV$

   c. $\mathrm{T\,dw} = \mathrm{d}Q_{rev} = dU + p\,dV$

   d. $\mathrm{T\,dQ} = \mathrm{d}Q_{rev} = dU + p\,dV$

   e. none of these

9. The change in entropy (∆S) upon heating 2 moles of an ideal gas from temperature T_1 and volume V_1 to temperature T_2 and volume V_2, at constant pressure, is

   a. $\Delta S = C_V \ln(T_1/T_2) + 2\,R \ln\left(\frac{V_2}{V_1}\right)$

   b. $\Delta S = C_p \ln(T_2/T_1) + 2\,R \ln\left(\frac{V_2}{V_1}\right)$

   c. $\Delta S = C_V \ln(T_2/T_1) + 2\,R \ln\left(\frac{V_2}{V_1}\right)$

   d. $\Delta S = C_V \ln(T_2/T_1) + 2\,R \ln\left(\frac{V_1}{V_2}\right)$

   e. none of these

10. The heat associated with a composite cycle ($Q_{composite}$) is related to the heats associated with its constituent cycles (Q1, Q2, Q3, …) as

    a. $Q_{composite} = Q_1 + Q_2 + Q_3 + \cdots$

    b. $Q_{composite} = Q_1 + Q_2 + Q_3 + \cdots > 0$

    c. $Q_{composite} = Q_1 + Q_2 + Q_3 + \cdots < 0$

    d. a and b

    e. none of these

11. Plot of ∆S on Y-axis vs ln (T_2/T_1) on the X-axis ($T_2>T_1$), for the heating of an ideal gas, at constant pressure (S, entropy; T, temperature) is

a. linear with negative slope

b. an exponential curve with growth

c. linear with positive slope

d. an exponential curve with decay

e. none of these

12. Plot of ΔS on Y-axis vs ln (V_2/V_1) on the X-axis ($V_2>V_1$), for the heating of 1 mole of an ideal gas, at constant pressure (S, entropy; V, volume; R, gas constant) is

a. linear with slope equal to - R

b. an exponential curve with growth

c. linear with positive slope equal to R

d. an exponential curve with decay

e. none of these

13. The change in entropy (ΔS) upon heating 2 moles of an ideal gas from temperature T_1 and pressure p_1 to temperature T_2 and pressure p_2, at constant volume, is

a. $\Delta S = C_p \ln(T_2/T_1) + R \ln(p_1/p_2)$

b. $\Delta S = C_p \ln(T_2/T_1) + 2R \ln(V/p_2)$

c. $\Delta S = C_p \ln(T_1/T_2) + 2R \ln(p_1/p_2)$

d. $\Delta S = C_p \ln(T_2/T_1) - 2R \ln(p_2/p_1)$

e. none of these

14. Plot of ΔS on Y-axis vs ln (p_2/p_1) on the X-axis ($p_2>p_1$), for the heating of 1 mole of an ideal gas, at constant volume (S, entropy; p, pressure; R, gas constant) is

a. linear with slope equal to - R

b. an exponential curve with growth

c. linear with positive slope equal to R

d. an exponential curve with decay

e. none of these

15. The change in entropy (ΔS) for an isobaric heating of 3 moles of an ideal gas from temperature T_1 to temperature T_2 is

a. $\Delta S = C_V \ln\left(\frac{T_2}{T_1}\right)$

b. $\Delta S = C_p \ln\left(\frac{T_1}{T_2}\right)$

c. $\Delta S = -C_p \ln\left(\frac{T_2}{T_1}\right)$

d. $\Delta S = -C_p \ln\left(\frac{T_1}{T_2}\right)$

e. none of these

16. Plot of ΔS on Y-axis vs ln (T_2/T_1) on the X-axis ($T_2>T_1$), for the heating of 2 moles of an ideal gas, at constant pressure (S, entropy; p, pressure; R, gas constant) is

a. linear with slope equal to – C_p and intercept zero

b. an exponential curve with growth with intercept zero

c. linear with positive slope equal to C_p and intercept zero

d. an exponential curve with decay with intercept equal to zero

e. none of these

17. The increase in entropy (ΔS) with respect to the standard state entropy (S˚) of 3 moles of an ideal gas at pressure of p atm is (R, gas constant)

a. $\Delta S = S_2 - S^{\circ} = -n\,R\ln(p/1\,atm)$

b. $\Delta S = S_2 - S^{\circ} = -3\,R\ln(p/1\,atm)$

c. $\Delta S = S_2 - S^{\circ} = 3\,R\ln(p/1\,atm)$

d. $\Delta S = S_2 - S^{\circ} = -3\,R\ln(p_2/1\,atm)$

e. none of these

18. At constant volume conditions, the following is true (C_v heat capacity at constant volume)

a. $T\,dV = C_V\,dT$

b. $T\,dp = C_V\,dT$

c. $T\,dq = C_V\,dT$

d. $T\,dS = C_V\,dT$

e. none of these

19. The following is true for all reversible processes,

a. $\Delta S = \frac{\Delta V}{T}$

b. $\Delta S = \frac{\Delta p}{T}$

c. $\Delta S = \frac{H}{T}$

d. $\Delta S = \frac{\Delta H}{T}$

e. none of these

20. The third law of thermodynamics allows us to calculate

a. heat capacity of a substance

b. internal energy of a substance

c. entropy of a substance

d. maximum work that can be extracted from a substance

e. none of these

14.14 Self Tests Key

1. a, 2. b, 3. c, 4. b, 5. d, 6. b, 7. d, 8. b, 9. c, 10. a, 11. c, 12. c, 13. d, 14. a, 15. d, 16. c, 17. b, 18. d, 19. d, 20. c.

14.15 Problems

1. A gas of 0.0418 moles expands against an external pressure of 12 atm isothermally at 700 K to six times its original volume. What is the accompanying entropy change? (Ans. 0.62 J/K)
2. A gas expands adiabatically from a pressure of 30 atm at 400 K from 0.1 L to 0.15 L. What are the number of moles, final temperature, final pressure and ΔS? (Ans. 0.0914 moles, 203.5 K, 10.175 atm, and -0.46 J/K)
3. Calculate final volume, mole numbers and change in entropy as an ideal gas expands from 40 atm, 0.2 L and 500 K to 2 atm and 300 K. (Ans. 2.4 L, 0.195, 2.79 JK)

4. What is the final temperature when the ΔS was 14.4 J/K as an ideal gas was heated under constant pressure conditions from 300 K? (Ans. 500 K)
5. Calculate Cp and ΔS when a gas of 0.1 mol was heated irreversibly under isobaric conditions from 300 K to 400 K? (Ans. 2.08 J/K, 0.598 J/K)
6. If 87.9 J/Kmol is the entropy of a gas at 100 atm and 300 K, what is its standard molar entropy at this temperature? (Ans. 126.2 J/K mol)
7. The latent heat of evaporation of liquid water at its boiling point is 540 cal/g. What is the increase in its molar entropy when the phase transition liquid water to steam occurs? (Ans. 108.99 J/Kmol)
8. Obtain the specific heats, transition temperatures from the internet and calculate the third law entropy of 1 mol of water at 300 K and 1 atm. (Ans. 69.9 J/K mol)
9. Discuss the arbitrary assignment of entropy of pure substances at zero K to be zero, considering this recent publication. Is this justified or not, explain in 100 words or less (A. M. Steane, On determining absolute entropy without quantum theory or the third law of thermodynamics, *New J. Phys.,* Volume 8, pp 043022, year **2016**.
10. Explain why you can't go back to your class yesterday, or can you? Use thermodynamic arguments, and entropy increases of the universe to make your arguments one way or the other.

Chapter 15. Entropy and Distributions

After completing this chapter, you will be able to:

- Use the spatial and energy distribution functions to estimate entropy.
- Establish the relation between entropy and the number of ways a system can be arranged
- Deduce the number of complexions or arrangements of an ensemble of particles
- Relate the number of arrangements and the volume of the system to its entropy
- Examine the possible arrangements of particles in available levels in the ensemble
- Relate the energy distribution to its entropy and relate it to the temperature

Goals

- Determine the probability of constructing a system of particles, the ensemble
- Synthesize an equation relating the number of configurations of the ensemble with its entropy
- Quantify the relation between entropy and volume, from special distribution functions
- Synthesize an expression for the distribution of particles in a system of energy levels and relate the function to entropy of the system.
- Deduce the relation between temperature and entropy from the energy distribution function.
- Reflecting on the relation between entropy of the system and the special/energy distribution functions.

15.1 Why Study This?

Entropy is demonstrated to be a key player in predicting if a chemical reaction or a physical process will occur spontaneously, in the previous chapter. This ability of entropy is due to its connection with the way the particles are distributed both in space and in terms of energy. Exploring this connectivity between entropy and distributions of volume/energy is important to gain further insight into why entropy is a key factor in driving spontaneous processes. This aspect of entropy and probability is extremely useful in qualitative explanations of why some processes occur spontaneously while others do not. From cocktail conversations to mechanistic investigations, discussions can center around the properties of entropy and its dependence on pressure, volume and temperature. The latter is one of the major reasons to study the current topic. In addition, entropy plays a very important role in our daily lives and understanding this connection can help make sense of what is happening in our environment or world of possibilities.

15.2 Probability and Entropy

We will first get a picture of what probability is and then figure out how we can distribute particles in a given volume. We all know that if we buy a lottery ticket, we are likely to win with certain probability. For example, if we buy no tickets there is no chance of winning the lottery. However, if we buy out all the tickets, of course, we are sure to win. So, we conclude that the probability (P) of winning the lottery is somehow related to the number of tickets we buy, and the number of tickets sold, under ideal conditions, of course.

$$\mathrm{P} = probability\ to\ win = \frac{number\ of\ tickets\ bought}{number\ of\ tickets\ sold}$$

Now, we consider a simple example into how this is applied for a practical example.

15.2.1 The coin toss

We ask, what is the probability that when we toss a coin three times, that heads will show up three times in a row? We know that every time we toss the coin, there is a 50 percent chance that the head will show up. If we do these tosses three times in a row, each event is independent of the other events, and each event has the same probability of heads showing up 50% of the time. If we do three tossups in a sequence, what is the probability that they head will show up three times in a row. We know for sure that this is not zero, but we also know that this will not happen each time. So, what is the probability of this event happening?

For each tossup, the probability from the above formula is ½. One outcome divided by two possibilities. If we toss the coin twice in a row, then the probability that both tosses will show heads is the product of the probability of the first event and the probability of the second. This is because the two events are independent and not related. That is, history has no bearing on the future outcome. Then, the probability is ½ multiplied by ½ and that is ¼.

Next, we compute the probability of tossing three times in a row and obtaining three consecutive appearances of heads. By extension of the above logic, we write that it should be ½ for each event multiplied by three such events and hence, it will be 1/8.

We use this approach of calculating independent probabilities for calculating the probability of obtaining a particular distribution in space or compute total number of possible distributions for several particles in a given volume. First, we will take simple systems where the volume and the number of particles is limited.

15.2.2 Bugs, boxes and entropy

Consider three bugs are to be placed in four boxes, and we want to know how many distinct ways we can arrange them. To solve the problem, certain rules are to be applied first. Rule one is that only one bug can occupy each box at any given time, this is called single occupancy rule (Figure 15.1). This is important because we will divide the available volume of the gas container into small volume cells that will fit just one molecule and not more. Thus, single occupancy is relevant, and we say that no two molecules will be at the same place at the same time.

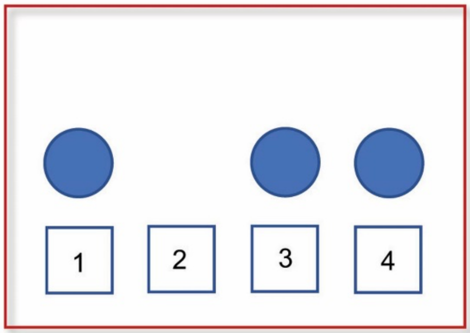


Figure 15.1 One of the arrangements of three bugs (blue dots) in four boxes (blue squares), chosen randomly.

The second rule is about the identity of any two bugs are the same or not. That is, we can't distinguish between any chosen bug and any other bug in the collection, then it is called the identical objects problem. This is also relevant for gas particle model. When the gas is pure, as we normally do, then no two gas particles can be distinguished from each other. Therefore, our second rule is that all objects of the collection are identical from each other (Figure 15.1).

15.2.3 The case of identical bugs and boxes

Now we work out how many possible ways we can distribute the three identical bugs in 4 identical boxes with single occupancy, but we number the bugs for the sake of counting them easily. For the first bug, we can choose any of the four boxes, because they are all empty, and hence, there are four distinct ways to choose the boxes for this bug. The second bug can be placed in any of the three remaining boxes (single occupancy) and hence, there are only three boxes to choose from. The third bug can be placed in any of the two remaining boxes and hence, there are only two choices to pick from.

Thus, the total number of ways to arrange them will be a product of these outcomes, which is 4x3x2, 24. Since the 3 bugs are identical, we will soon realize that some of the 24 arrangements are not distinct from the others or some outcomes will be counted more than once. That is, three bugs can be arranged among themselves in 3! ways, and hence the distinct configurations will be 24/3! or only 4 distinct configurations exist (Figure 15.2).

Thus, when the objects are identical, as in the case of a pure substance, we have fewer configurations, or so-called complexions. Thus, there are only 4 distinguishable ways we can arrange the three identical bugs in four single occupancy boxes. We also picked the number of boxes and bugs to be quite similar and this is more like close packing of the particles in a solid or a liquid with very little occupancies left over. In a gas sample, though, we recognize that there are lot more boxes than the bugs (particles) where each box is the size of a particle, and the entire available volume can be divided into these small boxes.

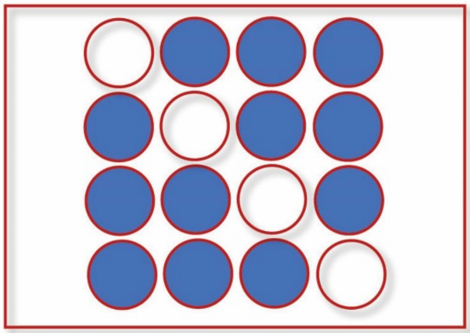
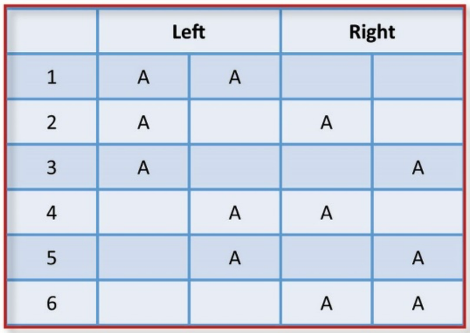


Figure 15.2 Distinct configurations of three bugs (blue dots) occupying four boxes (red circles) where each bug is identical to any other bug in the collection.

15.2.4 The congregational probability

Here, we will ask a related question. Having worked out how the bugs may be distributed in space we want to know what is the probability that all the particles will congregate in one half of the container. That is, we ask what is the probability that certain number of particles condense or aggregate, spontaneously?

In this case also, we pick identical bugs, but choose only two of them and divide our container into four boxes, where each box can only accommodate one bug. We choose small numbers for both variables, so that we need not count too many possible ways of distributing them. So, we want to know what is the probability that both bugs will appear on the same side of the 4 boxes of the container and not on opposite ends of the container (Figure 15.3).



	Left		Right	
1	A	A		
2	A		A	
3	A			A
4		A	A	
5		A		A
6			A	A

Figure 15.3 Distinct configurations of two bugs (blue dots) occupying four boxes (rectangle), where each bug is identical to any other bug and each box accommodates only one bug. Each row is a collection of four boxes, and a single complexion. Six complexions are shown. We will count how many of the complexions have both bugs on the right half, how may have both bugs on the left, and how many have one in each half.

This is the congregational probability, probability that the bugs will overwhelmingly congregate on one side rather than the other side. We will count the possibilities as shown in Figure 15.3. We place the first bug in the first box, and then place the second one in the box next to it (row 1). Now we keep the first bug in its location and move the second bug to the next box (row 2). Then, the second bug is moved to the third box, then we move it to the fourth box or the last box (row 3).

Now, all empty boxes are filled at least once by bug two. All of these are distinct configurations and ok to count. We keep the second bug in the second box and move the first bug to the third box (row 4). Then move it to the last box (row 5). Then, we move the second bug to the third box, keeping the first in the last box (row 6). This way we have created six distinct configurations and there are no more left to make.

For example, two bugs occupy 4 boxes in 4x3 or 12 ways, but the two identical bugs can be arranged in 2! ways among themselves. Thus, there should be only 6 distinct outcomes, as in Fig. 15.3. However, we chose to place them individually and move them around, so that we can get a picture of what is where exactly, and this is useful for the problem at hand.

Next, we examine the individual configurations shown in Figure 15.3 and count that there are 2 configurations out of the six that have both the bugs on the same side. Thus, 2 out of 6 configurations have the bugs congregating. There are 4 other configurations where each bug is on each side of the container or uniformly distributed.

From these, we can summarize that the probability that both bugs will be on the right side is 1 in 6 and the probability that both will be on the left side is 1 in 6, but it's important note that these two are equal because of the unusual symmetry of our box. However, the probability that the bugs will be more uniformly distributed is 4 in 6, much greater than 1 in 6 of their congregational probability.

So, bugs like to spread out, just as gas molecules, and this is just because of probability not because they like or they hate each other. The probability that the gas particles congregate on just one side is much less than that they will be uniformly distributed. This is analogous to the following example.

Consider a tank of compressed gas, and when the valve is open in the room, the gas molecules will spontaneously and quickly leave the tank and occupy the entire room. We normally never see that gas molecules of a room rush from the room and enter the tank and compress themselves to high pressures. We simply ask why? The above example illustrates the answer. The probability that the gas particles leave the pressurized tank and occupy the room is overwhelmingly larger than the probability that they all will condense or pressurize themselves in a gas tank all by themselves.

It may appear trivial that this should not be a problem, an everyday occurrence. But if we think about each molecule, each molecule has the equal probability of moving along the +x direction or -x direction +y direction or -y direction +z direction or -z direction. If the directionality of the molecule going left or going right is random, then why one direction is preferred so all the molecules travel out of the tank, into the room, but not in the opposite direction?

This is referred to as the Boltzmann paradox and that paradox is resolved very nicely using probability or the congregational probability and that's the reason to discuss the above example. There is an overwhelming probability that the gas molecules leave a pressurized tank of small volume and occupy the large space of the room, rather than the opposite event. As the room size increases, the number of boxes increase and the probability that bugs will spread out becomes more and more, and that the bugs will congregate becomes less and less probable. Thus, the natural tendency is to occupy all the space available.

Example 15.1

Examine entropy changes when hot gases expand during the combustion of the internal combustion engine of a car.

We define the cylinder with fuel filled before the spark plug ignites as the system, enclosed by the boundary of the gas separating the surroundings from the system. We choose this as an open system, so that we can add the fuel, spark the plug, and allow the work to appear at the boundary of the system as the piston moves to expand the gases. We heat the gases by igniting and burning the fuel with oxygen in the cylinder and transfer some energy to the surroundings. As the hot gases expand almost instantly, we can consider this as adiabatic expansion and the piston is moved up during this step, the masses are raised, or the crank shaft turns producing power to move the car. Expansion of the gases and increase in temperature due to the heat released during the combustion increase entropy of the system. The expansion is accompanied by increase in the number of complexions of the volume distribution and the increase in temperature produces an increase in the energy distribution and the combustion process is a spontaneous one. After this step of expansion and rotation of the crank shaft, the burnt gases are released into the environment (thus, polluting the air around) and certain gas mass is being moved out of the system and into the surroundings. Now, the entropy of the surroundings is also increasing, in addition to many other contributions including the waste heat, motion of the car, frictional losses etc.,

15.2.5 Number of complexions (Ω) and entropy

The above discussion will lead us to calculate the entropy of the system under consideration. The total number of possible, distinguishable, or unique complexions (Ω) is related to entropy through the Boltzmann constant (k), as following

$$S = k \ln \Omega$$

For four identical bugs in 4 identical boxes with single occupancy, there is only one complexion possible, Ω = 1, and S = 0. This is analogous to a perfectly crystalline, pure sample at 0 K. The third law states that entropy of the system should be zero, and our calculation from the distributions, agrees with that.

This relation is very powerful, because if we can figure out the total number of bugs and boxes we have, we can precisely calculate the maximum possible distinct configurations and from it the entropy of the system, a wonderful triumph of Physical Chemistry!

15.3 Spatial Distribution and Entropy

We will use the above approach to determine entropy of a gas occupying a vessel of finite dimensions and volume V. We divide the volume of the container of the gas into m boxes, where each box can accommodate only one particle (rule 1) and all particles are identical (rule 2). Since the size of the gas particle being very small, we will have very large number of imaginary boxes in our container. Let there be N number of particles in our gas sample and m boxes, each of which can accommodate only one gas particle. We get the number of complexions via a systematic approach delineated below, and from it we calculate the entropy of our system.

15.3.1 Case 1: Identical boxes, two particles

Let there be just 2 particles and we distribute them in volume V comprising of m boxes. The first particle can be placed in any one of the m boxes, and the second particle can go into any one of the remaining m-1 boxes. Then, the total number of complexions for two particles are m(m-1) but half of these will be identical to the other half. Then, the number of unique complexions (Ω) will be m(m-1)/2.

$$\Omega = m\,(m-1)/2$$

Entropy of the two-particle system and m boxes is given below.

$$\mathrm{S} = \mathrm{k} \ln \Omega = k \ln(m\,(m-1)/2)$$

The value of the logarithmic term will be very large, and hence the entropy of the system will be very high as well. Having worked out this simple case, we now move on to a system of N particles, and m identical boxes, as following.

15.3.2 Case 2: Identical Boxes, N identical particles

As before, we have m boxes in volume V occupied by N identical particles. The first particle can occupy any one of the m boxes, and hence, it can be arranged m different ways. The second particle can occupy any box out of m-1 remaining boxes and hence, can be arranged in m-1 ways. Then, the third particle can be arranged in m-1-1 or m-2 ways, the fourth particle in m-2-1 or m-3 ways, and so on. Then, the Nth particle can be arranged in m-N-1 ways. Note that the number of ways of arranging N particles is not m-N ways but m-N-1, because the particles that are placed before the Nth particle used up this many boxes. Thus, the total number of complexions will be a product of these terms divided by N! Because N particles can be arranged among themselves N! ways. Thus, the total number of distinguishable complexes are given as below.

$$\Omega = [m\,(m-1)\,(m-2)\ldots(m-\,(N-1))]/N!$$

By multiplying both the numerator and the denominator with (m-N)!, we simplify to the following.

$$\Omega = m!/N!(\mathrm{m\text{-}N})!$$

Entropy is then given simply as below.

$$S = k \ln \frac{m!}{N!\,(m-N)!}$$

This is a straightforward expression to calculate entropy, just using pencil and paper, and that is the strength of Physical Chemistry. You can sit down and think about it and in your mind's eye, you can work out the observable, then go to the lab and test if this is correct.

In summary, we constructed a very simple statistical model to determine the number of ways we can prepare the system, or ways we can arrange the gas molecules in a gas container. The logarithm of number of ways of distributing the particles in the volume is related directly to entropy, with a proportionality constant of k. As Ω increases, entropy also increases.

Example 15.2

Calculate the number of complexions of arranging 3 identical bugs in 5 identical boxes.

The first bug can be arranged in 5 ways, the second can be placed in any remaining 4 boxes, and the last into any one of the 3 boxes. Thus, number of distributions are 5x4x3 but the 3 bugs can be arranged in 3! ways, and hence the number of distinct configurations are 60/6 = 10.

15.3.3 Volume dependence of S – Gases

The dependence of entropy on volume and pressure, as indicated earlier, can be analyzed in terms of number of complexions, in a quantitative manner. We use the general formula, make necessary substitutions for pressure or volume changes and then compare the equations of entropy derived earlier.

$$\Omega = [m\ (m-1)\ (m-2) \ldots (m-\ (N-1))]/N!$$

We will simplify the above equation for gases by recognizing that the number of volume elements in our gas container (m) are much larger than the number of gas particles (N). This is because a small amount of gas occupies a large volume. There are large gaps between gas molecules at any given time. The actual volume of the gas particles is only a small fraction of the volume of the container, as we discussed it under the kinetic theory of gases.

Under these conditions, we can state that m>>>N, such that we can approximate that m-1 = m, m-2 = m, m-3 = m,….and m-N = m. Then each term in the numerator is m, with N-terms, as following.

$$\Omega = \frac{[m\ (m)\ (m) \ldots (m), N\ terms]}{N!} = m^N/N!$$

$$\mathrm{S} = \mathrm{k} \ln \Omega = k \ln\left(\frac{m^N}{N!}\right)$$

$$S = k\ (N \ln m - \ln N!)$$

Now, let the volume increase from the initial volume V_1 having the number of boxes m_1 to volume V_2 with number of boxes m_2, at constant T. Then ΔS is given as below.

$$\Delta S = \ k\ (N \ln m_2 - \ln N!) - k\ (N \ln m_1 - \ln N!)$$

Recognizing that the two ln N! terms can be cancelled, we obtain the following.

$$\Delta S = k\ N\ (\ln m_2 - \ln m_1) = k\ N \ln(m_2/m_1)$$

But, m is proportional to V, so we replace m_2/m_1 with V_2/V_1 to obtain the following.

$$\Delta S = k\ N \ln(V_2/V_1)$$

The desired expression for volume dependence of entropy, from the last chapter, has nR term while we have kN in the above expression. So, writing N = n M, where n is number of moles and M is the molecular mass, we recognize that kN = nR. Then we get the final expression with this substitution.

$$\Delta S = nR \ln(V_2/V_1)$$

Thus, starting from the number of complexions, we arrived at the effect of volume on entropy, which is independent of the derivation from the last chapter. Therefore, our expression for Ω and its relationship with S, must be correct. This is very cool because we are getting the same result from two very different approaches. Next, we examine the effect of pressure on entropy of gases.

Example 15.3

Calculate the change in entropy when the number of single occupancy boxes are increased from m to n for N identical boxes. Comment the cases when m=n, m>n, and m<n.

The change in the entropy is given as $\Delta S = k\,N\ln(m/n)$. When m>n, the ln term >1 and ΔS is positive, when m=n, the ln term reduces to 0, and when m<n, the ln term is negative. Thus, entropy decreases in the last case. These changes are within our expectations of the volume dependence of entropy at constant temperature and pressure conditions.

15.3.4 Pressure dependence of entropy - gases

We increase pressure by simply increasing n, at constant V and T. We add more and more gas to the same container or increase the number of particles to increase pressure. Let the number of particles increase from N_1 to N_2. Then, we write the change in entropy as following.

$$\Delta S = S_2 - S_1 = k\,[N_2\ \ln m - \ln N_2!] - k[N_1 \ln m - \ln N_1!]$$

Grouping like terms and taking k and ln m out and recognizing that the ln N! terms can be a ratio, we get the following simpler relation.

$$\Delta S = k\,[(\ln m)\,(N_2 - N_1) + \ln(N_1!/\,N_2!)]$$

Since m>>> N_1 or N_2, we can consider $N_1 = N_2$, the first term vanishes, and we are left with only the second term.

$$\Delta S \sim k\ \ln(N_1!/\,N_2!)$$

We recognize that pressure is proportional to N, and hence, proportional to N! and we get the final expression, as following.

$$\Delta S \sim k\ln\,(p/p')$$

Thus, pressure and entropy are inversely related, just as we expect from the previous chapter. Thus, we conclude in this section that our statistical approach agrees well with previous discussions. Now, we extend these arguments to liquids and solids.

Example 15.4

What is the change in entropy when the number of particles of a system are increased from N to M, at constant temperature and volume?

The entropy change is given by the expression $\Delta S \sim k\ \ln(N!/\,M!)$. Increasing the number from N to M, the ln term becomes negative and the entropy decreases. This is consistent with the deduction that increasing the number of particles at constant temperature and volume increases pressure, and entropy decreases with increase in pressure.

15.4 Liquids and Solids

First, the condensed phases have volumes much less than gases, and hence, there is not too much empty space between the N particles occupying m boxes. Then, m is approximately the same as N or that we can simplify our expression for the number of complexions, as following.

$$\Omega = \frac{m!}{N!\,(\mathrm{m-N})!}$$

$$\Omega \sim \frac{N!}{N!\,(\mathrm{N-N})!} \sim 1$$

Therefore, we conclude that when the number of boxes is nearly the same as the number of particles, our approach indicates that the entropy of the system is much less than that of the gases. This is true, experimentally. When the number of particles and the number of boxes approach each other, then the entropy approaches zero. Next, we examine the dependence of entropy on temperature or how it depends on thermal energy of the system.

15.5 Entropy and Energy Distribution

Since temperature is a manifestation of the thermal energy of the system, we need to examine how the energy is distributed among the particles. Thus, if we raise the temperature of the system then more particles will be associated with higher energy than at lower temperatures. Thus, we need to examine particle distribution among the energy levels at one temperature, and then figure out how the distribution would change when we raise or lower the temperature. Therefore, we will construct a ladder of energy levels, and then ask how the particles are distributed with respect to energy, instead of volume that we examined in the previous section.

15.5.1 Ladder of discrete energy levels

We will assume that our system has a series of energy levels where each level has a finite amount of energy. That means, if our particle occupies that level, it will have the corresponding amount of energy. These energy levels have different energies, and we assume that the energy spacing between the levels is the same and equal to some value, ε. This is important and matches with the harmonic oscillator model applied to a thermal oscillator, discussed in the quantum mechanical treatments of molecules. Along these lines, we will also set the lowest energy level to have non-zero energy or have zero-point energy, as dictated by quantum mechanics. Now, we have a system of energy levels (Figure 15.4) where each vertical red line corresponds to certain energy level of ε_1, ε_2, ε_3, ε_4, ε_5 …*etc.*, where each level is separated by energy interval of ε. The collection of N particles will have n_1 particles in level ε_1, n_2 particles in level ε_2, n_3 particles in level ε_3 and so on. Energy increases from the left to right, as indicated by the blue arrow.

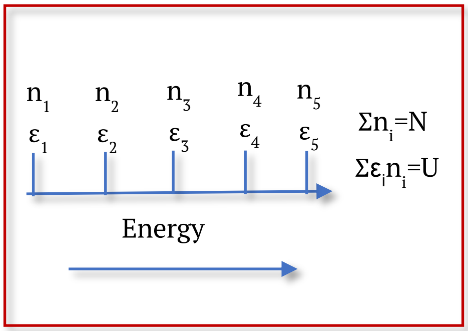


Figure 15.4 Energy levels (ε_1, ε_2, ε_3, ε_4, …) of a collection of N particles with a uniform separation of ε, where n_1 particles are present in level ε_1, n_2 particles in level ε_2, n_3 particles in level ε_3 and so on. The total number of particles is N and total energy of the particles is U.

We need to keep in mind that the total energy of the system (U) is finite and hence, sum of all energies of all particles should be equal to U. We recognize that the energy states are discrete, not continuous. One way to look at this is that you have a bucket of marbles, and you need to add them to different cups and there are many ways you can choose the marbles to add to each cup. With this understanding, we proceed to obtain the number of complexions.

15.5.2 Particle distribution into the first energy level

We begin adding particles to each energy level and we start with the first level and calculate the number of ways we can populate this level, first. We realize that level ε_1 can be filled in different ways with n_1 particles. We can add the first particle to this level, and we can choose that one particle from our collection of N particles in N different ways. Thus, we can choose that first particle in N distinct ways, and this leaves N-1 particles remaining to be distributed. The second particle can be chosen in N-1 ways to added to first energy level.

Then, the third can be chosen in N-2 ways to fill into this level and so on so forth, till the last particle corresponding to n_1 is chosen. That last particle can be chosen $(N-(n_1-1))$ ways. For example, the first particle is chosen in N-(1-1) = N and the second N-(1-2) = N-1 and so on, thus, the last particle can be chosen in $(N-(n_1-1))$ ways.

Thus, the first level (ε_1) is filled in N $(N-1)(N-2)\ldots.(N-(n_1-1))$ ways. This way, we will fill the second and subsequent energy levels, as discussed below.

15.5.3 Energy Distribution into the remaining energy levels

After choosing n_1 particles, we only have $N-n_1$ remaining to be distributed among the remaining energy levels, and we pick n_2 particles for the second energy level. We now fill all the levels as following.

The second level (ε_2) is filled in $(N-n_1)(N-n_1-1)(N-n_1-2)\ldots.(N-n_1-(n_2-1))$ ways.

The third level (ε_3) is filled in $(N-n_1-n_2)(N-n_1-n_2-1)(N-n_1-n_2-2)\ldots.(N-n_1-n_2-(n_2-1))$ ways.

The fourth level (ε_4) is filled in $(N-n_1-n_2-n_3)(N-n_1-n_2-n_3-1)(N-n_1-n_2-n_3-2)\ldots.(N-n_1-n_2-n_3-(n_2-1))$ ways, till all N particles are completely distributed.

We don't really have to know what the exact energy levels are, or know exactly what n_1, n_2, n_3 … are to get the total distribution. This is the beauty of mathematics.

15.5.4 Restrictions on the Energy Distribution

The above filling of the states must satisfy two restrictions: the total number of particles can't exceed N and total energy can't exceed U. Total number of particles satisfy the condition shown below.

$$\sum_{1}^{N} n_i = N$$

We calculate the energy associated with the energy level 1 by adding the energies of all the particles in that level and then the energy of the next level and then the next level and so on. The sum of all these energies of all the levels must equal to U. This approach is demonstrated by the following equation.

$$U = n_1\,\varepsilon_1 + n_2\,\varepsilon_2 + n_3\,\varepsilon_3 + \cdots = \sum n_i\,\varepsilon_i$$

While satisfying these restrictions, we fill all the particles in the available energy levels. Next, we will compute how many distinct different ways we can build such a system and that is our number of energy complexions for our system and define the entropy of the system arising from the energy distribution.

Example 15.5

Calculate the total energy of the system if each of the n energy levels are filled by 1 particle each, and if the energy levels are equally spaced with a constant spacing of E joules.

The total energy is given by the expression $U = n_1\,\varepsilon_1 + n_2\,\varepsilon_2 + n_3\,\varepsilon_3 + \cdots = \sum n_i\,\varepsilon_i$ but the energy levels are single occupancy. Then n1 = n2 = n3 =….= n. This simplifies the series as (n=1):

$$U = n\,\varepsilon_1 + n\,\varepsilon_2 + n\,\varepsilon_3 + \cdots = \sum \varepsilon_i$$

In addition, the levels are equally spaced by energy of E joules, or ε_1=0, ε_2=E, ε_3=2E, etc., The series then simplifies as following.

$$U = 0 + 1E + 2E + 3E \ldots = E(0 + 1 + 2 + 3 \ldots n) = n\frac{n+1}{2} * E$$

15.5.5 Energy Complexions and entropy

The number of ways the first two energy levels can be populated is the product of the number of ways of choosing the particles to populate the first energy level multiplied by that of the second one, as below.

$N(N-1)(N-2)\ldots.(N-(n_1-1))(N-n_1)(N-n_1-1)(N-n_1-2)\ldots.(N-n_1-(n_2-1))$

However, one catch is that some of these are not unique because n_1 particles can be distributed among themselves n_1! and the same with particles in other levels as well. Thus, division of the total product of possibilities by these additional numbers ensures that each microstate we create is distinct. Thus, we write the total number of unique complexions by dividing with the number of ways the particles can be distribute among themselves, as below.

$$\Omega = \frac{[N\,(N-1)\,(N-2)\ldots(N-(n_1-1))][(N-n_1)\,(N-n_1-1)\,(N-n_1-2)\ldots(N-n_1-(n_2-1))]..(2)(1)]}{n_1!\;n_2!\;n_3!\;n_4!\ldots}$$

We recognize that the numerator has N products and each term is less than the previous term by 1, and hence, the numerator is equal to N!. Using this result, we obtain a simpler expression, as below.

$$\Omega = \frac{N!}{n_1!\;n_2!\ldots}$$

$$S = \mathrm{k}\ln\frac{N!}{n_1!\;n_2!\ldots}$$

As we increase the temperature of the system, internal energy increases, and we will have more particles in the upper energy levels. But we have a constant number of particles when the gas mass is kept constant. Thus, some particles are moved out of the lower energy levels and move into the upper energy levels.

We recognize that as we move the particles into the upper levels from the lower levels, numerator does not change, because we are not changing the total number of particles, mass of the gas is kept constant. So, as we raise the temperature, values of n_1, n_2, n_3, n_4 …. change, which are only in the denominator. We still have the same ladder of energy levels, it is not that any new energy levels are being created, some particles are moved out of the lower levels and placed in the upper levels.

For example, when n_1 is decreased, some particles in this energy state are used to populate higher states, and so, in general, the populations in the lower levels are decreasing and the populations in the higher levels are increasing. Thus, n_1, n_2, n_3 may become smaller but the number of particles in the higher states increase.

$$\Delta S = n\,R\ln(T_2/T_1)$$

Therefore, this trend makes the denominator smaller while the numerator stays constant, and there will be a wider distribution of the particles. A decrease in the value of the denominator will increase S value, and hence, increase in T increases entropy. This conclusion is also consistent with the expression we got in the previous chapter, as shown in Figure 15.5.

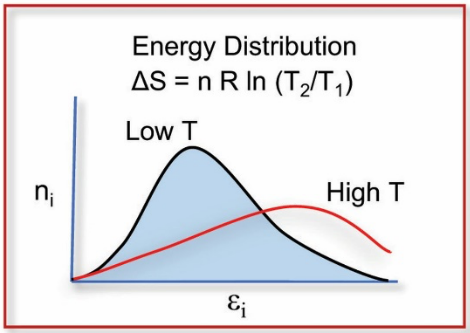


Figure 15.5 The change in the energy distribution curves when the temperature is increased from T_1 to T_2, where $T_2 > T_1$. The curve shifts from left (blue) to the right (red) and the height of the maximum point on the curve is reduced, simultaneously.

Example 15.6

If each energy level occupies a single particle, in a system of N particles, what is the temperature dependence of entropy?

The entropy change with respect to energy distribution is given by the expression: $S = \mathrm{k}\ln\frac{N!}{n_1!\,n_2!\ldots}$. When each level occupies a single particle, then each term in the denominator will reduce to 1 as each level is singly occupied. Then, the denominator equals to 1, and there is no dependence of entropy on the number of particles in each of the energy levels. If we move some particles from lower levels to higher levels by supplying energy, the entropy does not increase. Therefore, for this system, entropy is independent of temperature, and this deduction proves that in all substances that we know of, the restriction of single occupancy can't apply. Even if each level occupies two particles or 0 particles at a time, the entropy will be independent of temperature. Thus, only if each level can accommodate varying numbers of particles 0, or 1, or 2 or 3 or 4…., entropy depends on the temperature of the system.

The effect of temperature is illustrated, as we discussed earlier. At a lower temperature (T_1), we have the blue curve and when the temperature increases (T_2), the energy distribution curve shifts to the right (red) and the height of the maximum point on the cure is reduced, simultaneously. The curve is broadened by increase in temperature and this is consistent with shifting of the particles from lower energy levels to the higher energy levels, as we discussed above.

In summary, increasing the temperature, shuffles particles from lower levels to higher levels, thus broadening the distribution, increasing the number of complexions and thus, increasing of entropy of the system.

15.5.6 Physical significance

Next, we examine some examples. Gasses expand spontaneously from a high-pressure region to a low-pressure region. This is our common experience of spontaneous processes we encounter, such as wind blowing, hurricanes developing, etc. As the particles move from a high-pressure region to a lower pressure region, entropy is increasing. That's because as the expansion occurs, the volume distribution is increasing, the number of complexions is increasing and hence, entropy is increasing. Considering that the universe is a closed system, increase in entropy is a spontaneous process and these processes occur, naturally.

We examine the spontaneous flow of heat from high temperature to low temperature. This is because the loss of heat to a lower temperature region, the heat is dispersed more broadly. We have more states that are being populated. That is, greater spatial distribution of energy is achieved. For example, even when the volume is kept constant, the heat is released into the surroundings and the entropy of the system plus surroundings increases. Entropy of the universe, isolated system, increases and the heat flow is a spontaneous process.

Similarly, why does water flow down the hill and not up the hill, spontaneously? Water flows spontaneously from a higher region to a lower region, and as it flows down the hill, the kinetic energy of the water is increasing and part or most of it is converted to heat on its journey, and that heat is absorbed by the surroundings. Thus, the entropy of the system and surroundings is increasing. Thus, it is a spontaneous process. In this manner, we can understand how entropy increase in the system and the surroundings is responsible for the spontaneous processes we witness around us. However, this analysis with entropy is complicated by the fact that we need to pay attention to both the system and the surroundings to measure entropy changes (isolated systems only). Therefore, we continue to search, if there is thermodynamic property of the system, and only that of the system, that can predict if a process will be spontaneous or not.

Therefore, even though entropy turns out to be a champion in predicting spontaneous processes occurring in an isolated system, we need a property that can predict spontaneous processes in a closed or open system.

15.6 Molecular interpretation

The spatial and the energy randomness that we discussed in this chapter contribute to entropy, in a predictable manner. Expansion of gases to lower pressures is spontaneous because the molecular distribution in a larger volume produces more complexions and increases entropy of the system. When a gas expands, the interparticle distances are increasing, and thus, the number of boxes available for occupancy by the gas is increasing and hence, the number of complexions is increasing. Thus, the entropy of the system is increasing, and the process is spontaneous until it begins to compress the surroundings and an equilibrium is established when the system pressure equals to that of the surroundings.

At the molecular level, the increase in the energy of a system results in a broader distribution of energy and increases its entropy. However, gases do not spontaneously heat up, because some energy from the surroundings is to be obtained to increase the energy of the system, and this lowers the entropy of the surroundings. However, when the surroundings are at a higher temperature, then heat flow into the system is spontaneous, because the total energy distribution (system + surroundings) increases.

Thus, the special distribution and energy distributions of both the system and the surroundings need to be considered to deduce the spontaneity of a process. This is a limitation of entropy discussions.

15.7 Applications in daily Life

Entropy and its properties are of importance in daily life, as described above. The flow of water down the hill, the dropping of fruit by the trees, flow of heat from a hot reservoir to cold surroundings etc. When we add milk to our coffee in the morning it spontaneously begins to mix and this is an example of another spontaneous process, of course stirring helps speed up the process. Dissolution of solutes such as sugar in the coffee are spontaneous too. Disorder is a spontaneous process and overcoming the disorder is the non-natural process that we need to work on, daily to overcome. The natural tendency is for our dorm rooms to become disordered.

15.8 Key points

1. The definition of probability and the distinct ways of arranging objects are important. We always count non-identical configurations, called complexions.
2. The number of distinct ways of arranging n particles in m boxes is given by Ω.
3. Entropy is given as $S = k \ln \Omega$ where k is the Boltzmann constant, a fundamental law.

15.9 New terms and units

The number of distinct complexions, entropy, Boltzmann constant. The number of complexions has no units.

15.10 Self Reflection

1. Winning a lottery by buying a ticket is a probability thing. If we buy lots of lottery tickets, will the probability sum or multiply with each ticket purchased and why?
2. Imagine that you are working for a life insurance company in Hartford CT. You oversee assessing risk taken by the company when a client purchases life insurance policy. If probability of death of an individual due to few different causes are known, how would you calculate the net probability of death? How much % profit will the company make, based on your analysis, annually?
3. Plot the special distribution curve as the gas expands from a low volume to high volume, at constant temperature.
4. Plot the energy distribution curve as the gas is heated from a lower temperature to a higher temperature, at constant volume.
5. If all spontaneous processes are controlled by entropy and entropy is controlled by probability, as thermodynamics insists, how did you happen to enroll in the Physical Chemistry course or read this book?

15.11 Further Reading

1. https://ocw.mit.edu/courses/chemistry/5-60-thermodynamics-kinetics-spring-2008/video-lectures/lecture-8-second-law/
2. https://ocw.mit.edu/courses/chemistry/5-60-thermodynamics-kinetics-spring-2008/video-lectures/lecture-10-entropy-and-irreversibility/
3. https://ocw.mit.edu/courses/aeronautics-and-astronautics/16-01-unified-engineering-i-ii-iii-iv-fall-2005-spring-2006/thermo-propulsion/

15.12 Self Tests

1. The probability of winning the lottery by an individual is related to the number of tickets sold by the lottery as

a. directly proportional

b. inversely proportional

c. exponentially

d. quadratically

e. none of these

2. The probability of winning the lottery is

   a. directly proportional to the tickets purchased divided by the number of tickets sold

   b. inversely proportional to the tickets purchased divided by the number of tickets sold

   c. unrelated

   d. product of the tickets purchased, and the number of tickets sold

   e. none of these

3. The number of unique ways of arranging three identical bugs in four identical boxes (single occupancy) is

   a. 3

   b. 4

   c. 9

   d. 12

   e. none of these

4. When two identical bugs are randomly distributed into four identical boxes, which are placed in a row, the probability that both bugs will occupy the left half of the row is

   a. 2/4

   b. 3/4

   c. 2/6

   d. 1/6

   e. none of these

5. The number of complexions (Ω) of preparing a system and its entropy (S) are related through the Boltzmann constant (k) as

   a. $S = k \ln \Omega$

   b. $S = k \ln 1/\Omega$

   c. $S = \ln \Omega$

   d. $S = -k \ln \Omega$

   e. none of these

6. The number of complexions of a perfectly crystalline solid at 0 K is

   a. <1

   b. -1

   c. >1

   d. 1

   e. none of these

7. The number of complexions of arranging two particles in m identical boxes is

   a. m

   b. 2m

   c. m(m-1)/2

   d. m/(m-1)

e. none of these

8. The entropy of N particles distributed into m boxes is

a. $S = m\ln\frac{m!}{N!(m-N)!}$

b. $S = p\ln\frac{m!}{N!(m-N)!}$

c. $S = n\ln\frac{m!}{N!(m-N)!}$

d. $S = k\ln\frac{m!}{N!(m-N)!}$

e. none of these

9. The change in entropy (ΔS) when N particles occupying m_1 identical boxes increases to m_2 identical boxes is

a. $\Delta S = k\ N\ (\ln m_2 - \ln m_1)$

b. $\Delta S = k\ N\ln(m_2/m_1)$

c. $\Delta S = k\ N\ (\ln m_2 + \ln m_1)$

d. $\Delta S = k\ N\ (\ln m_1 - \ln m_2)$

e. none of these

10. The entropy change (ΔS) of an ideal gas when the number of particles in the container is increased from N to N' is

a. $\Delta S \sim k\ \ln\ (N + N')$

b. $\Delta S \sim k\ \ln\ (N' - N)$

c. $\Delta S \sim k\ \ln\ (N * N')$

d. $\Delta S \sim k\ \ln\ (N/N')$

e. none of these

11. The number of complexions of N particles occupying m boxes in the condensed phase is approximated as

a. $\Omega \sim \frac{N!}{N!(\mathrm{N}-\mathrm{N})!}$

b. $\Omega < 1$

c. $\Omega > 1$

d. $\Omega \sim 0$

e. none of these

12. If the energy of ith particle is ε_i in a collection of n particles, then total internal energy (U) of the system is

a. $U = \sum n_i\ \varepsilon_i$

b. $U = \sum n_i\ /\varepsilon_i$

c. $U = \sum n_i + \varepsilon_i$

d. $U = \sum \varepsilon_i/n_i$

e. none of these

13. The entropy of the system of N particles occupying n_1, n_2, n_3… n_i particles in a system of energy levels 1, 2, 3…. i is (k is the Boltzmann constant),

a. $S = \ln \frac{N!}{n_1!\, n_2! \ldots}$

b. $S = \mathrm{k} + \ln \frac{N!}{n_1!\, n_2! \ldots}$

c. $S = \mathrm{k}/\ln \frac{N!}{n_1!\, n_2! \ldots}$

d. $S = \mathrm{k} \ln \frac{N!}{n_1!\, n_2! \ldots}$

e. none of these

14. The expansion of gas particles at constant temperature is accompanied by

a. increase in entropy due to broader distribution of particle energies

b. increase in heat due to broader distribution of particle energies

c. increase in entropy due to a broader spacial distribution of the particles

d. both a and b

e. none of these

15.13 Self Tests Key

1. e, 2. a, 3. b, 4. d, 5. a, 6. d, 7. c, 8. d, 9. a or b, 10. d, 11. a, 12. a, 13. d, 14. c

15.14 Problems

1. What is the number of unique ways of arranging three identical bugs in four identical boxes (single occupancy)? (Ans. 4)
2. When two identical bugs are randomly distributed into four identical boxes, which are placed in a row, what is the probability that both bugs will occupy the left half of the row? (Ans. 1/6)
3. How would you construct a system of N particles distributed into L energy level whose entropy is independent of temperature? Give two examples, and L should be at least 1. (Ans. Single occupancy in L levels, in another L=1)
4. What is the total energy of the system where each level is of single occupancy and energy of the nth state is given by n2E? (Ans. n(n+1)(2n+1)/6)
5. What are the number of complexions (omega) for a porous solid of m boxes, where every other box is vacant? (Ans. (m!/((m/2)!)2)
6. How many folds should one decrease the number of particles in a system to double its entropy? (Ans. e2)
7. How many folds should the number of available boxes for single occupancy be increased to double its entropy? (Ans. e2)
8. What is the change in entropy when the number of particles (N) are doubled at constant pressure and temperature/ (Ans. 2 k N ln 2)
9. Average temperature of the universe is 2.73 K and increased 10-fold over the past 10 billion years. What is the increase in the entropy of the universe over this timespan? Use average mass of the universe to be 1053 kg, and composition of its mass is roughly 90% hydrogen and 10% He, mass of the rest of the elements can be neglected. (Ans. Average molar mass is 0.002 kg/mol, average number of moles of particles is 0.5x1056 mol; ∆S~ 10x1056 J/K mol, if the total number of moles of matter did not change significantly when H2 is converted to He)
10. What is the increase in the entropy of the universe, approximately, in one day? Can this be the reason why you can't go back to your class yesterday? (Ans. 2.7x1044 J/K mol)

Chapter 16 Spontaneity and Free Energy

After completing this chapter, you will be able to:

- Recognize the thermodynamic criteria of a spontaneous process.
- Recognize the Helmholtz free energy (A) and the Gibbs free energy (G) as new state functions.
- Evaluate both A and G as a function of pressure, temperature, and volume.
- Establish the absolute criteria required to predict the direction of a chemical reaction.

Goals

- Apply the Clausius inequality to a natural process and develop absolute criteria for the spontaneity of the process.
- Show that Helmholtz free energy (A) controls the spontaneity of a process under constant temperature conditions.
- Show that a process under constant temperature and pressure is favorable only when the Gibbs free energy decreases.
- Synthesize equations that describe the dependence of A and G on standard thermodynamic variables, p, V and T.

16.1 Why Study this?

Gibbs free energy (G) is the primary thermodynamic property that can predict successfully if a given process is spontaneous or not when the experiment is carried out under constant temperature and pressure conditions. G also provides an excellent access to predicting when equilibrium will be achieved and predict the precise value of the thermodynamic equilibrium constant. All spontaneous processes happening under constant temperature and pressure conditions, in the universe, are characterized by a decrease in the G value of the system, independent of the surroundings. Thus, this chapter describing discovery and properties of G are of immense importance both in chemistry as well as in the universe. These are strong and important reasons to study this section.

16.2 Spontaneity

We will continue our quest to discover thermodynamic quantities which drive natural processes such as entropy, but our goal is to find properties that depend only on the system and independent of the changes in the surroundings. Naturally, such a property would also predict if the forward direction of the process is natural or the reverse. For example, the thermodynamic quantities such as temperature, work, heat, internal energy, and enthalpy, all have been tested in our previous discussions. None of them can predict the spontaneity of a given process. So far, our champion has been entropy, which can predict if a given process would occur spontaneously or not, as an absolute standard. The only caveat is that the total entropy (system + surroundings) is the metric of importance, and we will have to monitor both the system and the surroundings, unless it is an isolated system. Isolated system is not convenient for most laboratory measurements and therefore, we are looking for any property of the system, and that of the system only, which can predict if a given process is spontaneous, without examining the surroundings. We begin with Clausius inequality and attempt to replace entropy with other state functions to achieve this goal.

16.3 The Clausius Inequality

We begin with the Clausius inequality because it predicts the spontaneity of a process with certainty, but our strategy is to find a way to replace entropy term in this expression with equivalent properties of the system that do not involve the surroundings.

$$T\,dS \geq dQ \qquad \text{all processes}$$

When the process is reversible, the equality sign is valid and when the process is irreversible, the greater than sign is valid. This applies to all processes and our first step is to apply the first law to examine it further. We replace, for example, dQ with dU – dw_{total} and get the following equation.

$$T\,dS \geq dU - dw_{total} \qquad \text{all processes}$$

The work dw_{total} includes the pressure-volume work and all other forms of work such as the mechanical, electrochemical, photochemical, or other forms. Since we focus on gases for most of our discussions, we will factor out the pV work and write all other forms of work separately, as dw_{other}.

$$T\ dS \geq dU + p_{opp}\ dV - dw_{other}$$

We will be clear that p_{opp} is the opposing pressure on the gas, dV is change in the volume of the gas and $-p_{opp}dV$ is the pV work. If we were to examine chemical reactions occurring in a battery, for example, we will be interested in the electrochemical work as part of the dw_{other}. For now, we take the TdS term to the right and write the following.

$$0 \geq dU + p_{opp}\ dV - dw_{other} - T\ dS$$

This is a powerful expression, because for all irreversible processes taking place, the sum on the right side of the inequality should be less than zero and for all reversible processes or equilibria, the equality sign applies. Still, there are terms in the above expression that require us to look in the surroundings to observe the changes. If we have only condensed phases, then p_{opp} dV will be small and can be neglected, as shown below.

$$0 \geq dU - dw_{other} - T\ dS \text{ (condensed phases)}$$

When we have only gases and have pV work as the only form of work, which is often the case with gases, then we can write the following expression.

$$0 \geq dU + p_{opp}\ dV - T\ dS \qquad \text{(pV work only, gases)}$$

All the above expressions still require evaluation of the system as well as the surroundings, and hence, we continue our search for a property of the system that will predict the spontaneity of a process. We will impose specific restrictions on the above general expression for gases, such as constant temperature or constant pressure or both, and then re-examine if we can write the above expression in terms of the property of the system alone without involving the surroundings.

16.3.1 Constant temperature conditions

We start with $T\ dS \geq dU - dw_{total}$ and rearrange both TdS and work terms to get the following.

$$dU - T\ dS \ \leq\ dw_{total}$$

We impose constant temperature conditions, isothermal processes, which is experimentally quite convenient to carry out (dT = 0). Then, we write dU-TdS as a single term, for all isothermal processes.

$$d(U - T\ S) \leq\ dw_{total} \qquad \text{(constant T)}$$

Since U, T, and S are all state functions, we replace the composite term (U – TS) with a new state function A, where A = U – TS, and get the following.

$$dA\ \leq\ dw_{total} \qquad \text{(A = U – TS)}$$

A is a new state function, the Helmholtz free energy. For all spontaneous processes at constant temperature and $dw_{total} = 0$, the change in this property of the system (dA) is less than zero. Thus, for the first time, we arrived at an inherent property of the system for spontaneous processes. We get three specific conditions.

$$dA = dw_{total} \qquad \text{equilibrium}$$

$$dA <\ dw_{total} \qquad \text{the system moves forward spontaneously}$$

$$dA >\ dw_{total} \qquad \text{the system moves in the reverse direction spontaneously}$$

A has the units of energy, the Helmholtz free energy, it is the difference between the internal energy and the TS energy, and it is the maximum amount of total work we can extract from the system during an isothermal reversible process. We recognize that this form of work can be pV work as well as all other forms of work, such as electrochemical work (batteries).

This is one of the reasons it is coined as the free energy. We can write three separate conditions, when $dw_{total} = 0$.

$$A < 0 \quad \text{forward process is spontaneous}$$

Decrease in A, sponsors the spontaneous process or the irreversible process. When there is no further decrease in A, then it reaches a minimum value.

$$dA = 0 \quad \text{equilibrium is attained}$$

When dA =0, the system is at equilibrium, and when the change in A is positive, then the reverse process is spontaneous.

$$dA > 0 \quad \text{reverse process is spontaneous}$$

Example 16.1

Discuss the change in Helmholtz free energy (ΔA) when gasoline burns in the cylinders of the car and the crank shaft turns propelling the car forward or in reverse.

A is indicative of maximum amount of all forms of work that can be obtained (W_{all}) which includes pV work that we are concerned about in this example. Since T and V are kept constant, p remains constant unless mole numbers change. Thus, A is often used to analyze explosive reactions such as gas combustion in an internal combustion engine or during a chemical reaction with increase in mole numbers. In our system, if the engine burns CH_4 in pure oxygen to produce water, we have the following:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

then the change in mole numbers is 3-3 or zero. The reaction is exothermic and hence raises the temperature to perform work. If we burn octane, instead, then the mole numbers increase dramatically (estimate this using a balanced chemical equation), and work is performed with the heat released and also due to the increase in the mole numbers. If the temperature and volume are held constant, then the pressure rises rapidly which then can perform work against an external load. The maximum amount of work that can be derived at constant temperature is the decrease in the Helmholtz energy of the system during the burn.

In summary, we discovered a new state function, A = U-TS, which can predict the direction of a spontaneous process ($dA < dw_{total}$) or the establishment of equilibrium (dA = 0). It combines the internal energy and entropy into a single term, and thus, we can evaluate the spontaneity of a process independent of the surroundings. The maximum amount of work that can be extracted in an isothermal reversible process is equal to – dA, the explicit negative sign is used to indicate that work appears in the surroundings during the process. The surroundings are not involved in evaluating A. One drawback of A is that we must carry out the process under isothermal conditions, but the pressure can change, this is an issue. Since most of the natural processes occur under constant T & p conditions, it is convenient to evaluate the changes under these conditions, next.

16.3.2 Constant temperature and pressure conditions

We start with the combination of the Clausius inequality and the first law, that we examined before.

$$dU - dw_{total} - T\,dS \le 0$$

Since we want to hold p constant, it will be convenient to split dw_{total} into pV work and dw_{other}, where the latter accounts for all forms of work other than the pV work, and we get the following.

$$dU + p_{opp}\,dV - dw_{other} - T\,dS \le 0 \qquad \text{all processes}$$

Under constant pressure conditions, we can adjust the p_{opp} to be equal to p and obtain the following.

$$-(dU + p\,dV - dw_{other} - T\,dS) \ge 0 \qquad \text{constant pressure}$$

We can write the differential form, as following.

$$-(dU + p\,dV - T\,dS) - dw_{other} \ge 0$$

By imposing constant temperature conditions, along with constant p, we group the U, V and S terms and obtain the following.

$$-d(U + pV - TS) - dw_{other} \ge 0 \qquad \text{constant T, p}$$

We replace U + pV - TS by a single variable G, for convenience, to get the following.

$$-dG \geq dw_{other} \qquad \text{constant T, p}$$

Since, U, p, V, T, and S are all state functions, G is must be a state function. The decrease in G is the maximum amount of work, other than pV work, that can be extracted from the system. When all work is pV work, we write the following.

$$-dG \geq 0 \qquad \text{constant T, p}$$

$$dG \leq 0 \qquad \text{constant T, p}$$

The change in G or the Gibbs free energy is negative for all spontaneous processes, or that the Gibbs free energy of the system decreases for a spontaneous process. This is the hallmark of all natural processes, under constant pressure and temperature conditions, when all work is the pV work. When there is no further decrease in G, equilibrium is achieved, and when the change in G is positive, the reverse process is spontaneous.

$$dG = 0 \text{ Equilibrium is achieved}$$

$$dG < 0 \text{ Forward process is spontaneous}$$

$$G > 0 \text{ Reverse process is spontaneous}$$

For finite changes, when w_{other} is zero, and involves only the pV work, at constant T and p, we get the following criteria for ΔG (Figure 16.1 and Figure 16.2).

$$\Delta G = 0 \text{ Equilibrium}$$

$$\Delta G < 0 \text{ Spontaneous processes}$$

$$\Delta G > 0 \text{ Reverse process is spontaneous}$$

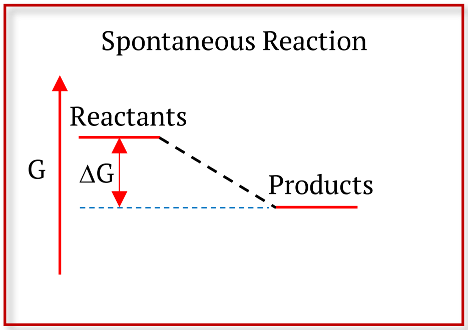


Figure 16.1 Changes in the Gibbs free energy of the system during a chemical reaction. When ΔG < 0, the forward process is spontaneous, and the reaction progresses converting the reactants to products, but the rate of the reaction is undefined.

The decrease in G provides the potential to drive the spontaneous processes down the hill, to take the analogy with the field of gravity, or that the negative gradient in G sponsors the forward process, and when there is no further decrease in G, the system reaches equilibrium. When the change in G is >0, then the reverse process is spontaneous.

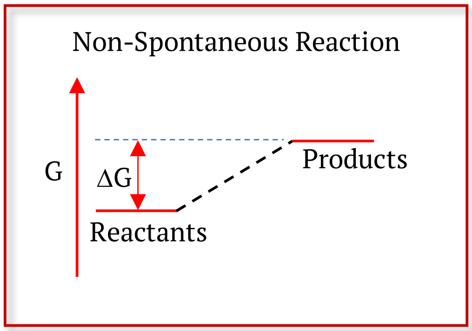


Figure 16.2 Changes in the Gibbs free energy of the system during a chemical reaction. When ΔG > 0, then the reverse reaction occurs spontaneously, and products are converted to reactants, but the rate of the reaction is unknown.

Example 16.2

Discuss the change in Gibbs free energy (ΔG) when gasoline burns in the cylinders of the car and the crank shaft turns propelling the car forward or in reverse.

We define the compressed gas of the cylinder filled with fuel, before the spark plug ignites, as the system and the boundary of the gas separates the surroundings from the system. The gases expand against a constant pressure. We choose this as an open system, so that we can add the fuel, spark the plug, and allow the work to appear at the boundary of the system as the piston moves to expand the burning gases. Some heat is transferred to the surroundings during the burn, but we can neglect that as the expansion is rapid. The burning of the gases is spontaneous because the G of the products, which are mostly carbon dioxide and water, is lower than the G of the reactants, gasoline, and oxygen. Although the expansion is rapid and nearly adiabatic, we can treat it as a two-step process with isothermal expansion followed by adiabatic expansion. During the isothermal expansion, the increase in mole numbers due to burn increase of pressure and temperature. System performs pV work at constant temperature. Then, in the second step, work is performed under adiabatic conditions where the interna energy of the gas is used to perform additional work. Thus, value of G decreases during these processes, as we will show that G decreases with decrease in pressure and decrease in temperature. Thus, the run of our car is a spontaneous process. That is, when we remove the foot from the brake pedal and apply it to the accelerator, gas is pumped into the cylinders, gas ignites, and work is produced to move the car forward or in reverse depending on the gear shift.

In summary, we finally arrived at a thermodynamic property that is only dependent on the system and a decrease in this property is characteristic of natural processes, under constant temperature and pressure conditions, when only pV work is involved. Its properties do not depend on the changes in the surroundings during the spontaneous process. G combines the enthalpy and entropy terms into one and hence, it can evaluate the spontaneity of a process, independent of the changes in the surroundings. This may be one of the highest achievements of the human mind. Finally, our quest is accomplished.

16.4 Properties of the Helmholtz free energy (A)

Helmholtz free energy is an intrinsic property of the system that is a measure of all work that can be extracted at constant temperature. Under constant temperature and volume conditions, it is the total amount of useful work (other than pV work) that can be extracted. This is useful for studying the electrochemical work that can be produced by a battery, for example. It is also useful in the study of explosive reactions where the pressure is not constant. The relation between A and temperature, as well as volume, are important considerations.

We start with our initial identity A = U – TS and write the differential form. Our goal is to examine how A depends on temperature first, and then on volume.

$$A = U - TS$$

$$dA = dU - TdS - SdT$$

We use the first law of thermodynamics, $dU = dq_{rev} + dw$, choose reversible processes ($dw = - pdV$) and replace dq_{rev} with TdS.

$$dU = dq_{rev} - pdV = TdS - pdV$$

We replace dU with these new terms, as follows.

$$dA = TdS - pdV - TdS - SdT$$

The TdS terms in the above cancel away, leaving a tidy small equation that connects A with changes in V and T.

$$dA = -pdV - SdT$$

We write the exact differential of A and obtain another tidy expression for A relating it to volume and pressure, as below.

$$dA = \left(\frac{\partial A}{\partial V}\right)_T dV + \left(\frac{\partial A}{\partial T}\right)_V dT$$

The exact differentials are of the property that the first and second terms in the above two equations of dA are identical. By comparing the corresponding terms, we write two separate relations, one of V and the other for T, as follows.

$$\left(\frac{\partial A}{\partial V}\right)_T = -p$$

$$\left(\frac{\partial A}{\partial T}\right)_V = -S$$

Therefore, the rate of change of A with respect to V, at constant T is equal to - p, and the rate of change of A with respect to T at constant V is - S. These equations are discussed further, below.

16.4.1 A as a function of V, for an isothermal process

The relation between A, V and p from the above section tells us that A and V are inversely related, and the proportionality constant is - p at constant T. As V increases, the value of A decreases and hence, the maximum amount of work that can be extracted also decreases. The proportionality constant is – p.

$$\left(\frac{\partial A}{\partial V}\right)_T = -p$$

Plot of A vs V at constant T is a curve, with a negative slope equal to the gas pressure (Figure 16.3, constant T). The plot is a curve because p itself is a function of V at constant T. The slope of the line is steep at low volume or high pressure, and the slope diminishes at larger volumes or low pressures.

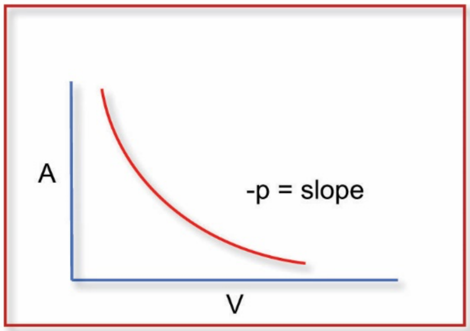


Figure 16.3 The decrease in Helmholtz free energy (A) with increasing volume is shown for a gas at constant temperature (red curve). The plot will not be linear, because pressure decreases with increase in volume at constant temperature.

When V increases in an isothermal process, pressure must decrease (Boyle's law), and the decrease in A ensures that it is a spontaneous process. Thus, compressed gas cylinder will leak out spontaneously into the room when the valve is open but the reverse process of gas from the room entering the cylinder and compressing itself is not spontaneous.

16.4.2 A as a function of T, for an isochoric process

Analysis of the relation between A and T, at constant V, provides insight into the behavior of A in an isochoric process. Helmholtz free energy is inversely related to temperature at constant V. The rate of change in A with T at constant V is equal to - S, as defined below.

$$\left(\frac{\partial A}{\partial T}\right)_V = -S$$

Thus, A decreases with increase in temperature with a proportionality constant equal to – S. Plot of A vs T at constant V is shown in Figure 16.4, and the slope is not constant, because S itself is a function of temperature and slope of the curve is negative due to the negative sign in front of entropy. The magnitude of slope is smaller at lower temperatures than at higher temperatures. Thus, curve bends downwards as opposed to the plot in Figure 16.3, which indicated upward curvature.

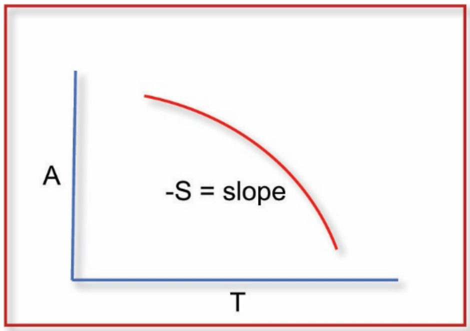


Figure 16.4 The decrease in Helmholtz free energy (A) with increasing T, at a constant V. The plot is not linear, because S increases with increase in T at constant V, and the curve is bent downwards.

Thus, the Helmholtz free energy decreases with temperature, in an isochoric process, the plot has negative slope at every point on the curve, and the slope keeps getting larger and larger with increase in T. The increase in slope is due to increase in S with increase in T. Since the decrease in A is greater than or equal to w_{total}, less and less amount of work is extracted at higher and higher temperatures, an important insight.

16.4.3 Mechanical Equilibrium

We will discuss the change in Helmholtz free energy (ΔA) to the attainment of mechanical equilibrium between two gas samples, when they are at different pressures. Let the two gas samples be separated by a movable wall, as in the steam box of a steam engine. Or, in the case of hurricane in the Atlantic where there is a pressure gradient with an imaginary wall separating the high-pressure and the low-pressure regions in the upper atmosphere. The following discussion is warranted.

Imagine that the gas is at higher pressure on the left of the wall (Figure 16.5) and at a lower pressure on the right of the wall. Due to the pressure differential, there will be a net force on the movable wall, and the wall moves from the high-pressure side to the low-pressure side, until the pressures on either side are equal (mechanical equilibrium). We ask why does this process happen spontaneously?

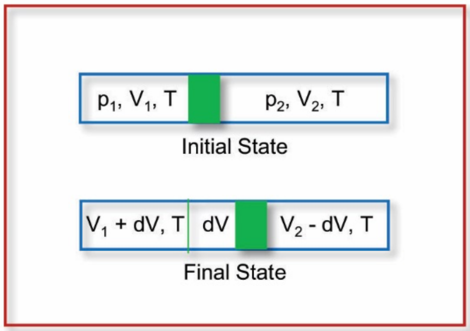


Figure 16.5 Mechanical equilibrium between two gas samples on either side of an imaginary wall separating the two regions of a gas sample. If the pressure on the left is greater than the pressure on the right, then the gas at higher pressure will spontaneously expand with a decrease in the Helmholtz free energy (A) at constant T. When the pressure on the right is higher, the opposite process happens spontaneously.

In the initial state (p_1, V_1, and T, upper part of Figure 16.5) is converted to the final state (p_2, V_2, and T) at constant T, or isothermal expansion, when $p_1 > p_2$. Let there be an infinitesimal expansion and let the volume increase on the left side by dV, inducing an infinitesimal decrease in pressure (-dp) (lower part of Figure 16.5).

On the right side of the wall, the volume decreases (-dV) as the gas expands on the left, with a corresponding increase in pressure by dp. In the final state, the green separation has been moved to the right. We will now analyze the change in A and decide if this process is spontaneous or not. If there is a decrease in A, then we know for sure that this is a spontaneous process, and dA =0 when the equilibrium is achieved.

Using the volume dependence of A at constant T, we write the following for the left side, where dA (left) is the change in A on the left side due to an infinitesimal increase in volume as it expands.

$$dA\,(left) = -p_1\,dV$$

Analogously, we write the change in the Helmholtz free energy on the right due to compression, as the following.

$$dA\,(right) = -p_2\,(-\,dV)$$

Therefore, total change in A, is the sum of the changes on the right and the left, and hence, we get the following (sign change due to parenthesis in the above expression).

$$dA\,(total) = (p_2 - p_1)\,dV$$

In the initial state, $p_1 > p_2$, the value in the parenthesis is negative, and dV >0. Therefore, A must decrease as the expansion of the high-pressure region proceeds while compressing the low-pressure region. Thus, the expansion is a spontaneous process, and gases must flow from a high-pressure region to a low-pressure region, all by themselves. This is also our common observation in daily life. So, for a spontaneous process to occur dA < 0 or – dA > 0, and hurricanes are driven by this change in the free energy of the system, under constant temperature conditions.

Example 16.3

What is the decrease in the Helmholtz free energy when a gas of 1000 L at pressure of 1.0 atm expands to 1100 L volume and a pressure of 0.9 atm, in kJ?

We use the formula $\Delta A = (p_2 - p_1) * (V_2 - V_1) = (1.0 - 0.9)\,atm * (1100 - 1000)\,L * 101.3\,\frac{J}{L\,atm} = 1.01\,kJ$

We can also predict when the equilibrium will be achieved in the above process. That is, A continues to decrease until there are no more changes in A, or dA = 0. From the above equation, we predict that this will be the case when $p_1 = p_2$ or when the two pressures on either side of the separation are equal. A mechanical equilibrium between the two gas samples is achieved.

Example 16.4

Discuss the birth and death of a hurricane in terms of changes in the Helmholtz free energy (ΔA).

We can apply ΔA to the creation and death of a hurricane. That is, the pressure gradient in the upper atmosphere is required for the formation of a hurricane and the hurricane ends when there is no detectable pressure gradient. We also notice that blowing of the wind on the ground is due to the pressure gradient across the surface of the globe. This pressure gradient, in turn, is created by solar heating of the surface of the planet, mostly the land mass. Similarly, there will be pressure gradients across the equator to the poles as well, caused by the seasonal changes.

The above expression is the reason gases are uniformly distributed in a container. This was one of our assumptions in the Kinetic Theory of Gases as well, as we recall. Thus, we seem to have come a full circle, but our analysis continues with Gibbs free energy, further. The latter is essential, because we want to keep both temperature and pressure constant in our experiments, for convenience, and test the conditions for spontaneity or equilibrium.

16.5 Properties of the Gibbs free energy

We will now examine the properties of the Gibbs free energy and how G is related to important experimental variables such as volume, temperature, and pressure. This is important because it is convenient to hold T and p constant and measure G in the laboratory, but G itself will be a function of these variables. Thus, a full analysis of this important thermodynamic variable is in order, particularly because it can predict if a chemical reaction will occur or will not, with certainty.

We use some calculus and common knowledge to pull this together. Using the definition of G, we first write it as a function of pressure, volume, and temperature in a rudimentary form. But this level of detail is not sufficient for further analysis. Thus, we write it in a differential form and then compare the terms with the exact differential of G, under specific sets of conditions. This way, we can readily obtain the various functions that we are interested in, as we did with the analysis of A, in the previous section.

$$G = U + p\,V - TS$$

In the differential form, we get multiple terms, two terms from each product, and write the following.

$$dG = dU + p\,dV + V\,dp - S\,dT - T\,dS$$

However, we recognize that we can replace U with q and pV terms (first law, pV work only) and test if we can simplify this long expression, as below.

$$dG = dQ_{Rev} - pdV + p\,dV + V\,dp - S\,dT - T\,dS \qquad (dU = dq_{Rev} - pdV)$$

Not that we use a reversible process ($dq_{reversible}$ and reversible pV work). This gives us a tidy relation, as following, after cancelling the pdV terms with opposite signs.

$$dG = dq_{reversible} + Vdp - SdT - TdS$$

After a closer examination, we recognize that the second law tells us that $dq_{reversible}$ = T dS, and using this relation, we can simply cancel the first and the last terms on the right side to get the final expression.

$$dG = Vdp - SdT$$

The last equation connects G with V, p, S, and T and this was obtained after substituting the first and the second laws into the definition of G. We now examine this in further detail, under constant pressure or constant temperature conditions to figure out how G depends on these two important experimental parameters.

16.5.1 G as a function of p and T

To proceed further, we need tidy relations between G and T, and between G and p. This we achieve by comparing the above differential expression with the exact differential of G. Because G is a state function, we can write its exact differential in terms of changes in temperature and pressure, as following.

$$dG = \left(\frac{\partial G}{\partial T}\right)_p dT + \left(\frac{\partial G}{\partial p}\right)_T dp$$

The sum of the above two terms on the right give the total change in G. The first term is the contribution to G only due to the change in temperature, pressure being kept constant. As discussed earlier, this term is the rate of change of G with temperature multiplied by the change in temperature (dT), at constant pressure.

The second term on the right is the change in G solely due to change in p, at constant temperature. This is the rate of change of G with respect to pressure multiplied by the change in pressure (dT) at constant T. Thus, we split the total change in G, as equal to the sum of two contributions, one from the temperature and the other from pressure. In the experiment also, it is convenient to vary one variable at a time to measure changes in the system.

We compare the two equations we got for dG and use the mathematical identity to deduce the equivalent quantities. That is, the temperature term in both equations should be identical, and we get the following, relating G with T at constant p.

$$\left(\frac{\partial G}{\partial T}\right)_p = -S$$

The rate of change of G with respect to temperature is given – S or that G is inversely related to the temperature with the proportionality constant equal to – S. In a similar manner as above, by comparing the pressure terms in the equations of dG, we get the following relating G with p, at constant T.

Example 16.5

What is the rate of change of Gibbs free energy with temperature, if the entropy of the ideal gas is 100 J/K?

The rate of Gibbs free energy per K = - S, and hence, it is 100 J/K. This quantity is like that of heat capacity, and in that sense, entropy is the decrease in the Gibbs free energy capacity and this also a function of temperature, and always negative.

$$\left(\frac{\partial G}{\partial p}\right)_T = V$$

The Gibbs free energy is inversely related to pressure, at constant temperature, and the proportionality constant being the volume of the gas. We will analyze the above two equations further, in the next section.

Example 16.6

What is the change in the Gibbs free energy when the number of moles of a system are doubled during a chemical reaction at constant volume and temperature (dU=0)?

When the mole numbers are doubled at constant temperature and volume, the pressure also doubles, assuming the ideal gas behavior. Then, ∆G also doubles and provides a thermodynamic potential to perform pV work.

16.5.2 G as a function of T, isobaric processes

Most of our transformations in the laboratory or in the environment around us, take place under constant pressure conditions, and this is very convenient for experimental evaluations. Thus, we ask how does G, the property that controls the spontaneity of a chemical reaction or physical process, depend on T for isobaric processes. For example, we could change the temperature of our system to make the reaction go forward or make it go in the reverse direction. Thus, chemists rely on this property to adjust the propensity and the direction of a chemical reaction at hand. Thus, a study of how G depends on T is of paramount importance to us for controlling the chemical reactions.

The rate of change in G with temperature, at constant p, equals to - S, as shown previously.

$$\left(\frac{\partial G}{\partial T}\right)_p = -S$$

Thus, G should decrease with increase in temperature due to the negative sign on the right side of the equation, and the magnitude of the slope of the plot of G vs T i negative (Figure 16.6). This derivative is interesting and can be compared with the first derivatives of U and H with respect to temperature, which are heat capacities, while the first derivative of G is related to the entropy of the system. Also, entropy and heat capacity have the same units. Thus, entropy is proportional to the Free energy capacity of the system, along the lines of heat capacity terms, an interesting insight into the nature of entropy.

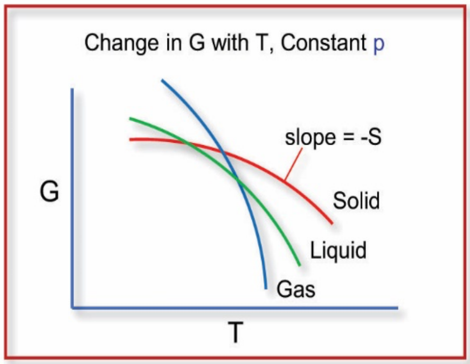


Figure 16.6 The decrease in Gibbs free energy (G) with increasing T, at a constant p (blue curve, gases). The plot is not linear, because S increases with increase in T at constant p. For the same reason, the curves for liquids and solids will be less curved, because entropy of gases increase with T, much faster than for the condensed phases (red curve). This curve for the condensed phases is also lower than that of the gases for the same reason.

Example 16.7

What is the change in the Gibbs free energy when the number of moles of a system are doubled during a chemical reaction under isobaric and isothermal conditions?

The reaction increases the number of moles, and hence, the volume increases at constant pressure and temperature. Thus, $\Delta G = V\, \Delta p - S\Delta T = 0$.

16.5.3 G as a function of T and the Gibbs-Helmholtz Equation

The temperature dependence of G at constant pressure is useful to calculate G at any other temperature, at constant pressure, by integrating the expression we got in the previous section. However, integration is not straightforward. We recognize that the slope of the rate of change of G with T involves entropy, and entropy itself is a function of temperature. Thus, we need to write S in terms of T for integration, and this path leads us to the famous Gibbs-Helmholtz equation.

$$\left(\frac{\partial G}{\partial T}\right)_p = -S$$

To write S in terms of T; H comes to rescue, and we use the relation G = H-TS to replace S, as following.

$$G = U + p\,V - T\,S = H - T\,S$$

$$-\,S = (G - H)/T$$

$$\left(\frac{\partial G}{\partial T}\right)_p = -\,S = \frac{G - H}{T}$$

The above expression is still not ready for integration, and we simplify this further. We examine differential of G/T with respect to T at constant p, as following. We get two terms.

$$\left(\frac{\partial G/T}{\partial T}\right)_p = \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_p - \frac{G}{T^2}$$

However, we just showed that the first derivative of G with respect to T is (G-H)/T and replacing the first derivative of G with respect to T in the above, we get the following simplified equation, after opening the brackets.

$$\left(\frac{\partial G/T}{\partial T}\right)_p = \frac{1}{T}\frac{(G-H)}{T} - \frac{G}{T^2} = -\frac{H}{T^2}$$

$$\left(\frac{\partial \Delta G/T}{\partial T}\right)_p = -\frac{\Delta H}{T^2}$$

We recognize that d(1/T) is (- $1/T^2$) dT and replacing dT with d(1/T) we get the final equation.

$$\left(\frac{\partial G/T}{\partial 1/T}\right)_p = H \quad and \quad \left(\frac{\partial \Delta G/T}{\partial 1/T}\right)_p = \Delta H$$

So, we can treat G over T as a variable and examine it as a function of 1/T. If H is a constant, we can integrate this expression. We have seen that H is only weakly dependent on temperature and hence, this assumption is valid over a short range of temperature. This is the Gibbs-Helmholtz equation. Plot of G/T vs 1/T gives a straight line, over a short temperature interval, with a positive slope equal to H (Figure 16.7). It gives us the rate of change of G/T with respect to 1/T.

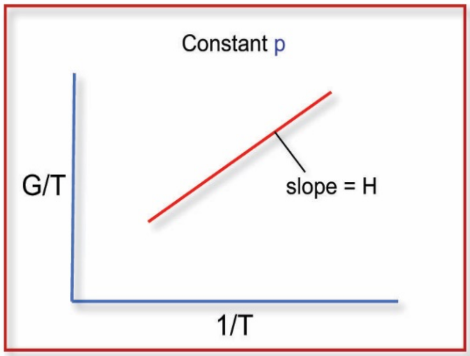


Figure 16.7 Plot of G/T as a function of 1/T, at constant p (red line). The plot is linear over a short interval of temperature with slope equal to H. Thus, G/T increases with 1/T, for all processes because H is always >0.

Although this is not exactly what we wanted, this is a form to examine how G varies with temperature. We adopt this equation to measure ΔH in the following form.

$$\left(\frac{\partial \Delta G/T}{\partial 1/T}\right)_p = \Delta H$$

$$\frac{\Delta G_2}{T_2} = \frac{\Delta G_1}{T_1} + \Delta H(\frac{1}{T_2} - \frac{1}{T_1})$$

By measuring ΔG as a function of temperature, we can obtain ΔH or by measuring ΔH either by calorimetric measurements or by equilibrium measurements at a series of temperatures, we can determine ΔG/T. Thus, we found a method to determine how G and ΔG depend on the temperature, and this is a key relation in thermodynamic analysis of equilibria or chemical reactions of interest.

In summary, we looked at the temperature dependence of G. But it is complicated as it involves entropy and found an alternate route where we can examine G/T or ΔG/T as a function of 1/T. This relates free energy changes with enthalpy changes via temperature, at constant pressure, which is very useful.

Example 16.8

Calculate ΔH when ΔG of the reaction decreases from -1 kJ/mol to -1.5 kJ/mol when the temperature is increased from 300 to 400 K, at constant pressure.

$$\frac{\Delta G_2}{T_2} - \frac{\Delta G_1}{T_1} = \Delta H\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \; or \; \Delta H = \left(\frac{T_1 T_2}{T_1 - T_2}\right)\left(\frac{\Delta G_2}{T_2} - \frac{\Delta G_1}{T_1}\right)$$

$$\Delta H = \left(\frac{300\ K * 400K}{300K - 400\ K}\right)\left(\frac{-1.5\ kJ/mol}{400\ K} - \frac{-1\ kJ/mol}{300\ K}\right) = 500\ J/mol$$

16.5.4 G as a function of p, ideal gas

Examination of the expression below connecting G and p at constant T, indicates that the slope of the plot will be positive and equals to the volume.

$$\left(\frac{\partial G}{\partial p}\right)_T = V$$

A plot of G vs p at constant T, should give a plot with a positive slope equal to V. Since V is also a function of p, the plot will be non-linear with a positive slope (Figure 16.8).

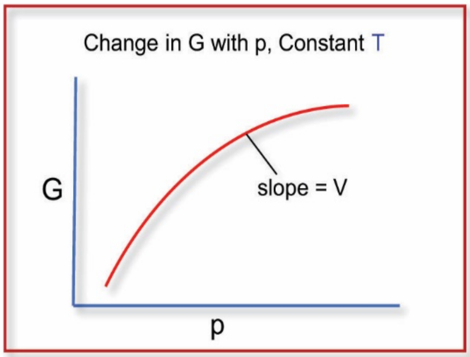


Figure 16.8 The increase in Gibbs free energy (G) with increasing p, at a constant T (red curve, gas). The plot is not linear, because the slope (V) decreases with increase in p at constant T.

We gain further insight into this expression by integrating it with appropriate limits, so that we can calculate G at any other pressure, when we know its value at a standard pressure. Rearrangement of the above terms gives us the following integral with limits 1 and 2.

$$\Delta G = \int_1^2 \mathrm{Vdp}$$

We attempt to integrate this equation, unlike the previous ones, and encounter that V itself is function of pressure, not a constant. However, for an ideal gas, we can replace V with nRT/p where T is a constant.

$$\Delta G = nRT \int_1^2 (1/\mathrm{p})\mathrm{dp}$$

We will set limit 1 to atmospheric pressure (p_0) and the upper limit to some other value, p. Integration with these limits gives the following.

$$\Delta G = nRT \int_{\mathrm{p0}}^{\mathrm{p}} (1/\mathrm{p})\mathrm{dp}$$

Upon integration, we get the logarithmic function because of p being in the denominator on the right, as below.

$$\Delta G = G_p - G_T^0 = n\,R\,T\ln(p/p_0)$$

Thus, G°_T is the value of G at any temperature T and pressure p_o, and from it we can calculate value of G_p at any other pressure p. When $p > p_o$, $G_p > G^{\circ}_T$. This equation can be obtained for any gas by performing the integration using the corresponding equation of state for the gas on hand. Thus, pressure increases Gibbs free energy for any substance, and provides higher potential to drive natural processes from.

Example 16.9

Calculate ΔG when an ideal gas of 1 mol expands from an initial pressure of 5 atm to a final pressure of 1 atm, at 300 K.

$$\Delta G = G_p - G_T^0 = n\,R\,T\ln(p_2/p_1)$$

$$\Delta G = 1\,mol * 8.31\frac{J}{K\,mol} * 300\,K * \ln\left(\frac{1\,atm}{5\,atm}\right) = -4.01\,kJ$$

16.5.5 Standard Gibbs free energy, ideal gas

In the above equation, we have written the limits G_p and $G^{\circ}_{(T)}$ corresponding to the limits p and p_o and we define the standard state at p_o = 1 atm, all pressures measured at temperature T. When the lower limit is 1 atm, then we have the ratio of the pressure at p atm to that of 1 atm, thus cancelling the units in the ln term, which is required mathematically.

$$\Delta G = G_p - G^0_{(T)} = n\,R\,T\ln(p\,atm/1\,atm)$$

$$G_p = G^0_{(T)} + n\,R\,T\ln(p\,atm\,/1\,atm)$$

Knowing G value at 1 atm and temperature T (standard free energy, $G^{\circ}_{(T)}$), we can calculate G at any other pressure and temperature T.

For solids and liquids, we can ignore the change in the volume over a reasonable range of pressures, because the coefficient of compressibility is too small, and we integrate the expression of G, directly with limits p_o and p, as following, at constant T.

$$\Delta G = \int_{p_0}^{p} \mathrm{V dp}$$

$$\Delta G = G_p - G^0_{(T)} = V\,(p - p_0)$$

Plot of ΔG vs ln p for condensed phases shows linear increase with a positive, constant slope of V, and G increases with p (Figure 16.9) with an intercept of 0.

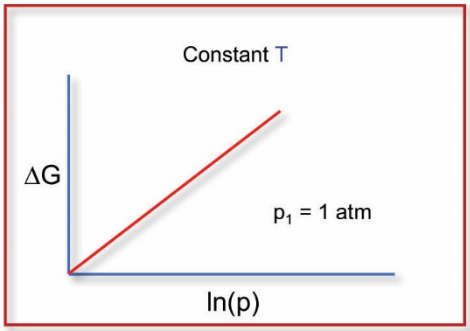


Figure 16.9 Plot of ΔG vs p for a condensed phase with a slope equal to V and intercept of 0, at constant T.

By examining the positive slope of the plot, we predict that the compression of condensed phases, as in the case of gases, is not a spontaneous process or that the de-compression of these phases is a spontaneous process. This phenomenon is the fundamental principle in p-the design and function of hydraulics which are important in aviation and the automobile industry.

Example 16.10

What is the change in the Gibbs free energy of water with a standard Gibbs free energy of 102 kJ/mol at 298 K when the pressure is increased at constant volume and temperature to 2000 psi in a power washer that is often used to clean decks and walls of a house?

The increase in pressure raises the Gibbs free energy and is given as $V(p\text{-}p_0)$. The pressure in psi is converted to atm by dividing with 14.695 psi/atm and use 0.018 L/mol as the volume of 1 mol of water.

$$\Delta G = V\,(p - p_0) = 0.018\frac{L}{mol}\left(2000\,psi * \frac{atm}{14.695\,psi} - 1\,atm\right) = 246\,J/mol$$

16.5.6 Standard Gibbs free energy in terms of fugacity

Because G is such an important property, we extend it to the discussion of real gases. Instead of worrying about which equation of state to use, we simplify the approach to make the correction for the non-ideal behavior, and introduce a new function called fugacity. Fugacity is to real gases as pressure is to the ideal gas. We simply replace pressure with fugacity (f) and obtain expression for ΔG for real gases. Fugacity has units of pressure, and we write the corresponding expression for real gases, as below.

$$\Delta G = G_p - G^0_{(T)} = n\,R\,T\ln(f/1\,atm)$$

Fugacity simply includes all non-ideal behavior of the gas into this one term. We write log of fugacity as equals to log of pressure and relate it to the compressibility factor (Z).

$$\ln f = \ln p + \int_0^P \left(\frac{Z-1}{p}\right)\,dp$$

When Z < 1, below the Boyle temperature, (Z-1)/p is negative, and fugacity is less than gas pressure. Above the Boyle temperature Z >1, and fugacity is greater than the gas pressure. Thus, we can account for the real gas behavior in our expression for Gibbs free energy by considering the experimental parameter ‘Z’ which depends on the characteristics of the individual gases.

In summary, we looked at the pressure dependence of G. It involves V and integration of this expression is straight forward for an ideal gas or for condensed phases. G increases with p, and this is the reason gases expand spontaneously from high-pressure to low-pressure region, but not the other way around. Accommodation is made for real gases by introducing fugacity, which is the equivalent to pressure of the ideal gas. Fugacity can be either greater than the gas pressure or less than the gas pressure, depending on the value of the compressibility factor. The latter depends on temperature, and hence, a thorough analysis is possible.

16.6 Equations of Thermodynamics

We write certain useful equations, as extensions of what we derived in this chapter, and these are useful for additional discussions of free energy terms. We begin with internal energy and write it under constant pressure conditions when all work is only pV work.

$$U = q - pV$$

We then, express enthalpy in terms of internal energy, as following.

$$H = U + pV$$

From the definition of Helmholtz free energy, we write the following.

$$A = U - T\,S$$

From the definition of Gibbs free energy, we write the following, after substituting for A and then replacing U + pV with H.

$$G = U - T\,S + p\,V$$

$$G = H - T\,S$$

$$G = U + pV - T\,S = A + pV$$

16.6.1 The combination of the first and the second laws

Substituting the second law into the first law, we get a very powerful relation which is often the starting point for the derivation of many thermodynamic relations (reversible process, pV work only, constant p).

$$dU = dq_{rev} - p\,dV$$

$$TdS = dq_{rev}$$

Combining the above two equations, we get the powerful relation, shown below.

$$dU = T\,dS - p\,dV$$

Complete differentiation of H and substituting dU, we get the expression below.

$$H = U + pV$$

$$dH = dU + p\,dV + V\,dp$$

Substituting dU = TdS – pdV in the above, we get a simpler relation.

$$dH = T\,dS - p\,dV + p\,dV + V\,dp$$

$$dH = T\,dS + V\,dp$$

Complete differentiation of A and substitution for dU, a compact expression for dA is obtained.

$$A = U - T\,S$$

$$dA = dU - T\,dS - S\,dT$$

$$dA = T\,dS - p\,dV - T\,dS - S\,dT$$

$$A = -p\,dV - S\,dT$$

Complete differential of G, and substitution for dU gives the following.

$$G = H - TS = U + p\,V - T\,S$$

$$dG = dU + p\,dV + V\,dp - T\,dS - S\,dT$$

$$dG = V\,dp - S\,dT.$$

In summary, we got the following equations that are useful for problem solving.

$$dU = dq + dW$$

$$dU = dq_{reversible} - p\,dV$$

$$dS = dq_{reversible}/T$$

$$dU = T\,dS - p\,dV$$

$$dH = T\,dS + V\,dp$$

$$dA = -p\,dV - S\,dT$$

$$dG = V\,dp - S\,dT$$

Finally, we write the exact differentials of the state functions to complement the above relations.

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT$$

$$dH = \left(\frac{\partial H}{\partial p}\right)_T dp + \left(\frac{\partial H}{\partial T}\right)_p dT$$

$$dS = \left(\frac{\partial S}{\partial p}\right)_T dp + \left(\frac{\partial S}{\partial T}\right)_p dT$$

$$dS = \left(\frac{\partial S}{\partial V}\right)_T dV + \left(\frac{\partial S}{\partial T}\right)_V dT$$

$$dA = \left(\frac{\partial A}{\partial V}\right)_T dV + \left(\frac{\partial A}{\partial T}\right)_V dT$$

$$dG = \left(\frac{\partial G}{\partial T}\right)_p dT + \left(\frac{\partial G}{\partial p}\right)_T dp$$

16.6.2 Cross Rule/Maxwell's Equations

The above thermodynamic relations are used with the cross rule to write additional equations (Maxwell's equations), shown below. Please consult your mathematics primer to learn about the cross rule. The fundamental equation and the corresponding result of applying the cross rule are demonstrated below.

$$dU = TdS - pdV \rightarrow\rightarrow \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$$

$$dH = TdS + Vdp \rightarrow\rightarrow \left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$$

$$dH = -pdV - SdT \rightarrow\rightarrow -\left(\frac{\partial p}{\partial T}\right)_V = -\left(\frac{\partial S}{\partial V}\right)_T$$

$$dG = Vdp - SdT \rightarrow\rightarrow \left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T$$

All the above equations are applicable to a variety of circumstances, their memorization is not recommended, they all can be derived from the first and second laws, and we must be careful to apply them but be aware of how we derived them.

16.7 Standard Gibbs free energy of Formation

The Gibbs free energy of formation is the difference in the free energies of the substance and its corresponding elements. Standard free energy is measured at 1 atm, at a specified temperature, usually at 25 ˚C (Table 16.1). The standard free energy of formation of all pure elements is set to zero, and those of the corresponding compounds are calculated from a table of standard enthalpies and absolute entropies of the corresponding elements that produce the substance of interest.

$$\Delta G_f^0(any\ compound) = \Delta H_f^0 - T\Delta S_f^0$$

$$\Delta H_f^0 = \Delta H_{f,produts}^0 - \Delta H_{f,reactants}^0$$

$$\Delta S_f^0 = \Delta S_{f,produts}^0 - \Delta S_{f,reactants}^0$$

Table 16.1 Standard Gibbs free energies of formation of a few substances at 25 ˚C, 1 atm.

Compound	*Formula*	*ΔG_f˚ (kJ/mol)*
Diamond	C	2.90
Graphite	C	0
Ammonia (g)	NH_3	-16.4
Ethanol	C_2H_5OH	-174.8
Water (g)	H_2O	-228.61
Carbon dioxide	CO_2	-394.39
Ozone	O_3	163.2

Example 16.11

Calculate the standard Gibbs free energy of formation of water at 25 ˚C, using its standard enthalpy of formation and standard entropy of formation values.

$$\Delta G_{f,water\ at\ 298.15\ K}^0 = \Delta H_{f,water\ at\ 298.15\ K}^0 - T\Delta S_{f,water\ at\ 298.15\ K}^0$$

Consider the reaction, $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ and we need to calculate the standard enthalpy and entropies of formation of water using this equation. The large negative value is impressive.

$$\Delta H_{f,water}^0 = (-241 - 0 - 0)\ kJ/mol$$

$$\Delta S^0_{f,water} = 188.84\frac{J}{K\ mol}$$

$$\Delta G^0_{f,water\ at\ 298.15\ K} = -241\frac{kJ}{mol} - 298.15\left(188.84\frac{J}{K\ mol}\right) = -298.1\ kJ/mol$$

16.8 Molecular Interpretation

Gibbs free energy successfully predicts the direction of a process, under constant temperature and pressure conditions. The system likes to lose this kind of energy, and when a reaction occurs spontaneously, the products are more stable with respect to this kind of energy when compared to the reactants. So, we ask what is this energy at the molecular level? This is the difference in energy between enthalpy and TS energy. We consider enthalpy as the total amount of energy to make a molecule and the energy needed to create the space for it to exist. TS is the energy related to the randomness of the system and hence, G is the intrinsic energy of making the system minus this penalty of energy associated with the randomness of the system that we created.

The energy associated with the randomness is a penalty because this term has the negative sign. Thus, we realize that when we take a certain molecule with all the potential and kinetic energy associated with its structure and motion, and convert this molecule to another molecule, we may expend some of the intrinsic energy (H) but certain amount of penalty also applies. This comes in the form of TS energy. It appears that all of enthalpy is not available for this conversion of the reactant to the product. That is the TS energy. Thus, simply decreasing the enthalpy of the molecule is not sufficient to drive a reaction, we must also pay a penalty in terms of the entropy change and when the sum of these two expenditures is met, the reaction can progress. Thus, reactions can be enthalpy controlled (ΔH compensates for the TΔS penalty) or entropy controlled (entropy change dominates) or controlled by both, but both contribute to the propensity of the chemical reaction as defined above. In simple terms, TS energy is very important for controlling the direction of the process, which is often not discussed in chemistry. Thus, when a chemical reaction or a physical process occurs spontaneously, the energy reserves of the molecule are used to some extent to lower its enthalpy sufficiently to overcome any unfavorable decreases in entropy, unless the process is driven by favorable entropy changes.

16.9 Applications in daily Life

The three laws of thermodynamics, that we discussed so far, are foundation stones for our discussions of thermodynamics and their applications in real life as well as in practical applications. These are fundamental arguments for gaining a better understanding of the world around us. The decrease in free energy (G or A) is essential to drive the natural processes that are occurring around us. Thus, when an apple falls from the tree, under constant p and T conditions, the Gibbs free energy is decreasing, and the reverse process must increase this kind of energy, which is not a spontaneous process. But this kind of energy is equal to enthalpy less the TS energy, and by knowing change in Gibbs free energy, we can determine if the system will move forward or in the reverse direction or at equilibrium. We designed several experimental methods to measure the change in this kind of energy directly, without examining the surroundings.

When the stone rolls down the hill and reaches the valley below, it is lowering this kind of energy and the reverse process increases the free energy of the system. Thus, measurements of G or A are essential in our understanding of natural processes around us, and this analysis explains why natural processes are natural!

16.10 Key points

1. The free energy is an important concept in chemistry and Helmholtz free energy is a measure of all the work that can be extracted from a system under constant temperature conditions, while Gibbs free energy is a measure of all the work that can be extracted, other than pV work, under constant p and T conditions.
2. The natural processes that we witness around us are driven by a decrease in G, and they stop when no further decrease in G is possible. G combines the enthalpy and entropy terms into one quantity.
3. Equilibrium is achieved when ΔG = 0, at constant temperature and pressure.
4. G decreases with decrease in p at constant temperature.

5. G depends on both H and S, as G = H – TS or ΔG = ΔH – TΔS.
6. G decreases with increase in volume at constant T.
7. The dependence of G on T is more complicated to study because this depends on entropy, but a work around gives the Gibbs-Helmholtz equation.
8. We arrived at many key thermodynamic equations that originated by combining the first and the second laws of thermodynamics.

16.11 New terms and units

Helmholtz free energy, Gibbs free energy, and fugacity. Both A and G have the units of energy, ergs, joules, calories etc., Fugacity has the units of pressure.

$$dA = -pdV - SdT$$

$$dG = Vdp - SdT$$

$$\frac{\Delta G_2}{T_2} = \frac{\Delta G_1}{T_1} + \Delta H(\frac{1}{T_2} - \frac{1}{T_1})$$

$$G_p = G^0_{(T)} + n\,R\,T\ln(p\ atm\,/1\ atm)$$

$$\Delta G = G_p - G^0_{(T)} = n\,R\,T\ln(f/1\,atm)$$

$$\ln f = \ln p + \int_0^P (\frac{Z-1}{p})\ dp$$

$$\Delta G^0_f(any\ compound) = \Delta H^0_f - T\Delta S^0_f$$

16.12 Self Reflection

1. Explain why most chemists prefer using Gibbs free energy for discussing spontaneity of chemical reactions, but not the Helmholtz free energy?
2. Explain the spontaneous flow of heat from high temperature to low temperature using Gibbs free energy parameter.
3. What does the ratio ΔA/ΔG teach us?
4. Given the space of your dorm room, list several processes that are downhill, in terms of Gibbs free energy and list at least one process that is up hill.
5. If spontaneous processes on this planet are due to decrease in G, how do the non-spontaneous processes occur?
6. If spontaneous processes are accompanied by decrease in G, where does that energy end up and how does it manifest?
7. Plot G vs U, G vs T, A vs p and A vs q.

16.13 Further Reading

1. https://ocw.mit.edu/courses/chemistry/5-60-thermodynamics-kinetics-spring-2008/video-lectures/lecture-13-gibbs-free-energy/

2. https://ocw.mit.edu/courses/chemistry/5-111-principles-of-chemical-science-fall-2008/video-lectures/lecture-18/13.6

3. https://chem.libretexts.org/Textbook_Maps/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical_and_Theoretical_Chemistry)/Thermodynamics/Energies_and_Potentials/Free_Energy/Gibbs_(Free)_Energy

16.14 Self Tests

1. The requirement for a spontaneous process, under constant T and pressure conditions is

a. release of heat

b. decrease in enthalpy

c. decrease in internal energy

d. decrease in Gibbs free energy

e. none of these

2. Increase in entropy is a hallmark of a spontaneous process in

a. an open system

b. closed system

c. isolated system

d. both a and b

e. none of these

3. A decrease in the Gibbs free energy change

a. of the system and the surroundings is the requirement for a spontaneous process

b. of the system is the requirement for a spontaneous process

c. of the surroundings is the requirement for a spontaneous process

d. both b and c

e. none of these

4. The hallmark of equilibrium at constant pressure and temperature is

a. $\Delta H = 0$

b. $\Delta U = 0$

c. $\Delta G = 0$

d. both a and b

e. none of these

5. The following is true for only spontaneous processes

a. $T\,dS \geq dU - dw_{total}$

b. $T\,dS \leq dU - dw_{total}$

c. $T\,dS \geq dU + dw_{total}$

d. $T\,dS \leq dU + dw_{total}$

e. none of these

6. The Clausius inequality is

a. $p\,dS \geq dQ$

b. $T\,dS \geq dQ$

c. $T\,dS \leq dQ$

d. $T\,dS \geq -dQ$

e. none of these

7. At constant temperature, the following is true for all processes (A=Helmholtz free energy)

a. $dA \;\leq\; dq_{total}$

b. $dA \;\leq\; dG_{total}$

c. $dA \geq\; dw_{total}$

d. $dA \;\leq\; dw_{total}$

e. none of these

8. The reverse process is spontaneous when

a. $dA > dq_{total}$

b. $dA > q_{total}$

c. $dA > w_{total}$

d. $dA > dw_{total}$

e. none of these

9. Under constant T and p conditions, the following is true

a. $-dG \geq 0$

b. $dG \geq 0$

c. $dG \leq 0$

d. both a and c

e. none of these

10. When ΔG =0, the system is

a. unstable

b. at equilibrium

c. far from equilibrium

d. can't say

e. none of these

11. The exact differential of A (Helmholtz free energy) with respect to V and T is

a. $dA = \left(\frac{\partial A}{\partial V}\right)_T dV + \left(\frac{\partial A}{\partial T}\right)_V dT$

b. $dA = \left(\frac{\partial A}{\partial V}\right)_p dV + \left(\frac{\partial A}{\partial T}\right)_V dT$

c. $dA = \left(\frac{\partial A}{\partial V}\right)_V dV + \left(\frac{\partial A}{\partial T}\right)_T dV$

d. $dA = \left(\frac{\partial A}{\partial V}\right)_T dV + \left(\frac{\partial A}{\partial T}\right)_V dT$

e. none of these

12. The plot Helmholtz free energy vs volume at constant temperature

a. is a line with positive slope

b. is a rising exponential

c. is a line with no slope

d. a vertical line

e. none of these

13. Plot of the Helmholtz energy vs temperature at constant volume has

a. a slope equal to entropy

b. a slope of zero

c. a slope of –(entropy)

d. can't say

e. none of these

14. The condition for mechanical equilibrium, at constant temperature, between two regions of pressure p_1 and p_2 is

a. when the two volumes are equal

b. when the two pressures are equal

c. when the two temperatures are equal

d. can't say

e. none of these

15. The following is correct

a. $dG = Vdp + SdT$

b. $dG = Vdp/SdT$

c. $dG = Vdp - TdS$

d. $dG = Vdp - SdT$

e. none of these

16. Plot of G vs T at constant pressure is

a. an upward curve over a small range of pressures

b. a downward curve over a small range of temperatures

c. linear with a positive slope over a small range of temperature

d. linear with a negative slope only for liquids

e. none of these

17. Plot of G vs temperature at constant pressure has a slope equal to

a. entropy

b. –(entropy)

c. enthalpy

d. – (enthalpy)

e. none of these

18. Plot of G/T vs 1/T at constant pressure has a slope equal to

a. ΔG

b. ΔS

c. ΔH

d. ΔU

e. none of these

19.The slope of the plot of Gibbs free energy vs pressure, at constant temperature, is

a. ΔH

b. ΔS

c. ΔV

d. V

e. none of these

20. A plot of ∆G vs ln(pressure), for an ideal gas, has

a. no slope or intercept

b. no slope

c. slope equal to V

d. slope equal to -V

e. none of these

16.15 Self Tests Key

1. d, 2. d, 3. b, 4. c, 5. e, 6. b, 7. d, 8. d, 9. d, 10. b, 11. d, 12. e, 13. c, 14. b, 15. d, 16. e, 17. b, 18. c, 19. d, 20. c

16.16 Problems

1. The standard enthalpy of formation of carbon dioxide is -393.52 kJ/mol and its standard entropy is 213.79 J/K mol, under ambient conditions. What is its Gibbs free energy of formation? (Ans. 457.3 kJ/mol)
2. What is the pressure required to raise the Gibbs free energy of liquid of 1 mol of 25 L, 1 atm by 25 kJ/mol? (Ans. 10.87 atm)
3. The Gibbs free energy of an ideal gas was raised by 10 kJ/mol of 1 mol at 300 K and 1 atm, by applying pressure at constant temperature. What is the pressure applied? (Ans. 56.1 atm)
4. Increase in temperature from 300 K to 400 K changed ∆G of the reaction from 1 kJ/mol to -0.5 kJ/mol, what is ∆H of the reaction, assuming it is constant over this temperature range? (Ans. 5.5 kJ/mol)
5. What is the entropy of the reaction when ∆G changes by -1.24 L atm/mol when the temperature was increased from 300 to 400 K? (Ans. 1.26 J/ K mol)
6. What is the change in the Gibbs free energy when the pressure of an ideal gas of 1 L was increased from 1 atm to 2.32 atm at 300 K by increasing the mole numbers? (Ans. 133.7 J)
7. When a reaction was carried out under constant temperature conditions, the initial volume of 1 L at 1 atm pressure increased to 5 L at 3 atm pressure. What is ∆A? (Ans. 8 L atm)
8. If the entropy of an ideal gas is 2.533 J/K mol, what is the change in Helmholtz energy when the gas is heated from 300 K to 500 K, under isochoric conditions/ (Ans. -5 L atm/mol)
9. What is the minimum temperature needed to drive a reaction forward if the enthalpy of the reaction is 238.11 J and ∆G of the reaction is 33.44 J at 300 K, under constant pressure conditions, assuming enthalpy is independent of temperature over this range? (Ans. >349.45 K)
10. Design an approach to determine the ∆G for a reaction under ambient conditions.

Chapter 17. Chemical Potential

After completing this chapter, you will be able to:

- Recognize the chemical potential (μ) as a state function for chemical applications.
- Use the chemical potential to predict the spontaneous direction of a chemical reaction.
- Calculate the chemical potentials of substances as a function of their concentration, pressure, and mole fractions.
- Define the molar entropies, enthalpies, and volumes of mixing and apply them to chemical reactions and physical processes.

Goals

- Show that chemical potential is a state function and relate it to other thermodynamic properties.
- Define chemical potential of a mixture as a function of the mole fractions of each of the components of the mixtures.
- Determine the changes in the chemical potential as a function of reaction progress.
- Synthesize equations relating the chemical potential with pressure, temperature and volume.
- Derive expressions for changes in the chemical potential, free energy, entropy, enthalpy, and volume for the formation of a mixture and then as a function of its composition.

17.1 Why Study this?

Most chemical reactions occur in finite proportions. A chemical equation, for example, indicates that certain moles of A react completely with certain moles of B completely to give rise to exactly certain moles of products C, D, *et cetera*. By this convention, we can measure ∆G of the reaction by simply subtracting the molar free energies of reactants multiplied by their stoichiometries from the molar free energies of products multiplied by their respective stoichiometries. Reactions seldom go to completion, and there could be limiting reagents, or the equilibrium may be established before the reaction can be completed. Even when we start with a single pure reactant, the chemical reaction renders it impure as time progresses, even if a single product is formed. As the reaction progresses by an infinitesimal amount, for example, we have a mixture of a small amount of product in a large amount of reactant and as the reaction continues, the composition of the mixture keeps changing till the reaction is complete. At the end of the reaction, we could still have a mixture of products, or products and leftover reactants. Even when a single product is produced, often the reaction is not complete as it stagnates at the equilibrium point. Thus, very few reactions produce 100% pure product at the end of a chemical reaction. Therefore, we need to consider that the formation of a mixture is a fundamental process in the progress of most chemical reactions.

Therefore, instead of using free energy per gram or per kilogram, it's more convenient for chemists to use free energy per mole of the substance under consideration and express this as a function of the composition of the reaction mixture. Thus, molar free energy or chemical potential is useful as another state function, and it has high significance, not just a mathematical convenience. We also recognize that while G is useful to study pure substances, chemical reactions require the analysis of mixtures. Hence, we need to examine how G varies with composition or how the chemical potential changes with composition. Therefore, the chemical potential is a key parameter that we use in determining the propensity of a chemical reaction and its direction.

Oftentimes, we start the chemical reaction as a mixture of reactants and end up with a mixture of products. There could be some leftover reactants in the reaction mixture or achieve equilibrium between the reactants and the products. So, oftentimes, we're dealing with mixtures of substances in chemistry. Thus, we examine the thermodynamic parameters in the context of a mixture to accurately assess the spontaneity of a chemical reaction from this vantage point.

17.2 Chemical Potential

The rate of change of Gibbs free energy with composition is the chemical potential of a substance and it varies with the composition of the mixture. Thus, we now examine G as a function of mole numbers in a chemical reaction, and one simple approach toward this goal is to express the change in the free energy of the reaction mixture using the exact differential for G with the mole numbers of the reaction components.

These may be reactants, products, or a mixture of both. Thus, change in G with respect to the changes in the mole numbers of the reaction components (n_1, n_2, n_3…) are written in the following manner:

$$dG = \left(\frac{\partial G}{\partial T}\right)_{p,n_1,n_2,\dots} dT + \left(\frac{\partial G}{\partial p}\right)_{T,n_1,n_2,\dots} dp + \left(\frac{\partial G}{\partial n_1}\right)_{p,T,n_2,n_3,\dots} dn_1 + \cdots$$

By writing the above, we assume that all work is of pV work as the reaction progresses, and we have already examined the first and the second terms of the above equation in previous sections. The remaining terms need explanation.

The third term is the rate of change of G with respect to the mole numbers of component 1, when we keep p, T, and the mole numbers of all remaining components constant, multiplied by the change in the mole numbers of component 1 (dn_1). This term gives the total contribution of component 1 to the change in G, as we change n_1. The next term involves the rate of change in G with respect to dn_2 multiplied by dn_2, at constant p, T, and when all other mole numbers are kept constant. The rest of the terms in our sum are like these terms. Hence, a discussion of the third term can be applied to these other terms with suitable changes. Thus, the exact differential is written as a rate of change with respect to the composition of the mixture, p, and T. This can be viewed as describing a multi-dimensional surface with tangents drawn parallel to specific pairs of axes, and each derivative is the slope of that tangent. At constant p and T, the first two terms are reduced to zero and we get the following:

$$dG = \left(\frac{\partial G}{\partial n_1}\right)_{T,p,n_2,\dots} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{T,p,n_1,\dots} dn_2 \dots$$

To simplify writing this long equation, we introduce a new state function (μ) as the rate of change in G with respect to the mole numbers of the substance of interest, while all other mole numbers, T, and p are kept constant.

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_1,\dots except\ n_i}$$

Now, we immediately obtain the following sum from the previous equation.

$$dG = \mu_1\, dn_1 + \mu_2\, dn_2 + \mu_3\, dn_3 \dots = \sum \mu_i\, dn_i$$

In the above, μ_i is the chemical potential of the ith term and it is the change in G with respect to the change in the composition (mixture) of all the components. Now, we examine the behavior of the new state function, chemical potential, which we defined as the rate of change of Gibbs free energy with respect to mole numbers of the mixture. The plot of G vs n_i, when all other variables are kept constant (Figure 17.1), provides us μ_i of the ith component, and it is the slope of the tangent drawn at any point corresponding to a given value of n_i.

Example 17.1

Discuss the change in chemical potential when gasoline burns in the cylinders of the car and the crankshaft turns, propelling the car forward or in reverse.

In this open system, we add the fuel, spark the plug, and allow the work to appear at the boundary as the burning gases expand. Oxidation of the fuel to carbon dioxide, and water, reduces the chemical potential of the system. This example illustrates the advantage of μ over G for our discussion because the mole numbers of substances are no longer required. When the net change in the chemical potential is decreasing, the car moves forward or in reverse depending on the gear shift.

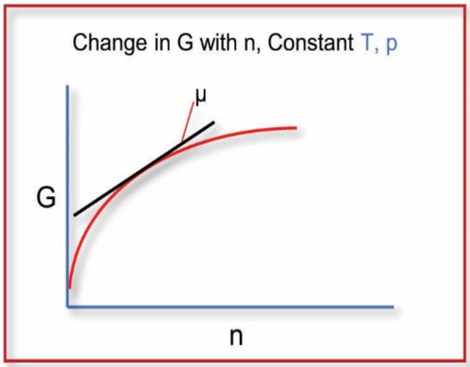


Figure 17.1 Change in the free energy as a function of the mole number (n), at constant T, p, and V (red curve). The slope of the tangent (black line) at any point gives the corresponding chemical potential of the substance.

We arbitrarily chose a curve in the above plot. It need not be a curve or a curve of this type, but it should have a positive slope at each point and G should vanish when all values of n are set to zero (limiting condition). When μ_i is independent of n_i, the plot will be linear with a constant positive slope.

Since G or n_i can't be negative, the slope of the tangent at any point will always be > 0. As μ_i is the rate of change of G with respect to n_i, it is also the molar free energy, or it is the change in the free energy of the mixture when one mole of component i is added to a large mixture such that the change in the mole numbers of the other components is negligible.

It is analogous to adding one mole of sodium chloride to an ocean of water and measuring the change in the free energy. By adding one mole of sodium chloride, we assume that we are not changing the concentrations of the other components of the ocean or pressure or temperature. Since the ocean has many moles of water, the change in the concentration of other components in the ocean is negligible by this act. However, the change in the free energy of the ocean due to adding this additional sodium chloride is the chemical potential. It is the G for one mole of the substance or the molar free energy of the substance (G/n). Thus, the definition of chemical potential is quite interesting.

In summary, we defined chemical potential as G over n or (G/n) or as the rate of change of free energy with mole numbers of the components of the mixture.

17.2.1 Gibbs free energy of a mixture

The above definition of chemical potential provides us with a unique opportunity to compute the total G of a mixture at constant T, p, and V by simply integrating the above expression with appropriate limits. Let us assume that all the mixture of volume V is enclosed inside a sphere of finite diameter. The shape of a sphere to enclose the mixture is chosen for convenience of integration, and the result will be independent of the shape of the container (Figure 17.2).

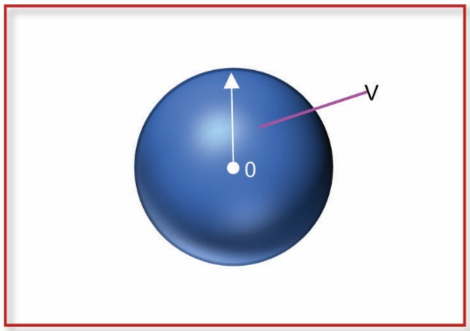


Figure 17.2 The integration sphere of volume V to obtain G of the mixture. The lower limit of integration is the point at the center with zero volume and the final limit is the total volume, V.

At constant temperature and pressure, we wrote the exact differential for change in G when the composition is changing. Now we integrate this expression with proper limits to get the free energy of the mixture.

$$\int dG = \int \sum \mu_i \, dn_i = \mu_i \int \sum dn_i$$

When the chemical potentials of all the components in the mixture are independent of the composition of the mixture, then we can take μ_i out of the integral. We start with zero volume at the center of the sphere, then increase the volume to V so that we can enclose the entire mixture within this volume (Figure 17.2). Thus, the value of the integral on the left side of the above equation is G of the mixture minus G of 0 volume. Integration of dn_i from 0 to V gives n_i, when μ_i is a constant. Thus, integration gives the following:

$$G_{mixture} - 0 = \int \sum \mu_i \, dn_i = \sum \mu_i \, n_i$$

$$G_{mixture} = \sum \mu_i \, n_i$$

Gibbs energy of a mixture, therefore, is simply the sum of the products of the chemical potentials of the constituents of the mixture multiplied by their respective mole numbers. We recognize that the value of G depends on the mole numbers as well as the chemical potentials of the substances in the mixture. In the next section, we dig a bit deeper into the nature of the chemical potential.

Example 17.2

Calculate the free energy of a mixture of two ideal gases of 1 mol each with chemical potentials of 25 J/mol and 33 J/mol, at 5 atm and 300 K.

$n_1=1$; $n_2=1$, $\mu_1= 25$ J/mol; $\mu_2= 33$ J/mol; T=300 K and substituting in the following, we get the answer.

$$G(mixture) = \mu_1 \, n_1 + \mu_2 \, n_2 = 25 \frac{J}{mol} 1 \, mol + 33 \frac{J}{mol} * 1 \, mol = \; 58 \, J$$

In summary, we showed that the chemical potential of the mixture is the sum of the chemical potentials of individual components of the mixture weighted by their respective mole numbers.

17.2.2 Chemical potential as a function of pressure

Since G is a function of pressure at a constant temperature, so will be the chemical potential. We start with the equation for G and work our way toward the pressure dependence of the chemical potential as follows:

$$dG = V \, dp - S \, dT$$

At constant temperature, dT =0 and so we get just one term.

$$dG = V \, dp$$

Integrating this expression with the limits of p and 1 atm, as we did earlier, we get the following for an ideal gas, where p is expressed in atm.

$$\Delta G = n \, R \, T \ln(p/1 \; atm)$$

We recognize that μ = (G/n) and write the following relation between chemical potential and pressure.

$$\Delta G/n = \mu - \; \mu^0 = R \, T \ln(p/1 \, atm)$$

Here, μ^0 = chemical potential at 1 atm, and $\mu - \mu^0$ is the change in the chemical potential as we change the pressure from 1 atm to p atm, and re-write the above as the following, popular form:

$$\mu = \mu^0 + \; R \, T \ln p$$

Thus, the chemical potential of a substance increases with pressure, just as the Gibbs free energy, and a plot of μ versus ln p for an ideal gas (Figure 17.3) has an intercept of μ° on the Y-axis, which corresponds to the chemical potential at 1 atm with a slope of RT.

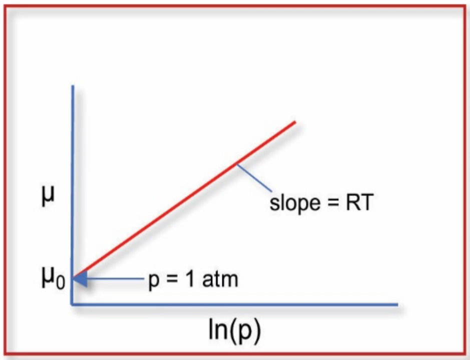


Figure 17.3 Chemical potential of an ideal gas as a function of pressure. The slope is equal to RT and the Y-intercept is the chemical potential at 1 atm.

Example 17.3

Calculate Δμ when a gas of 1 mol expands from an initial pressure of 5 atm to a final pressure of 1 atm, at 300 K.

p_1= 5 atm, p_2=1 atm, T=300 K, and substituting in the equation below, we get the answer.

$$\Delta\mu = \Delta G/n = (G_p - G_{p_0})/n = RT\ln(p_2/p_1)$$

$$\Delta\mu = 8.3144\frac{J}{K\ mol} * 300\ K * \ln\left(\frac{5\ atm}{1\ atm}\right) = -39.6\ J/mol$$

For real gases, we simply replace pressure with fugacity, as we did earlier, and get the following:

$$\mu = \mu^0 + RT\ln f$$

In summary, the chemical potential of a pure substance increases with pressure and hence, the reverse process (expansion) is spontaneous. Thus, gases expand from a high-pressure region to a low-pressure region to decrease their chemical potential, spontaneously.

17.2.3 Condition for concentration equilibration

We ask, what drives mass transport across a concentration gradient of a solute dissolved in a suitable solvent? These are not gases, but the topic will be useful later. Consider container A that has a concentrated solution of substance and separated from a dilute solution of the same solute present in container B. Let the two containers relate to a stopcock and when it is open, both solutions are brought in contact (Figure 17.4). The solute diffuses from higher concentration region A to lower concentration in container B, spontaneously. We will analyze this process using chemical potential.

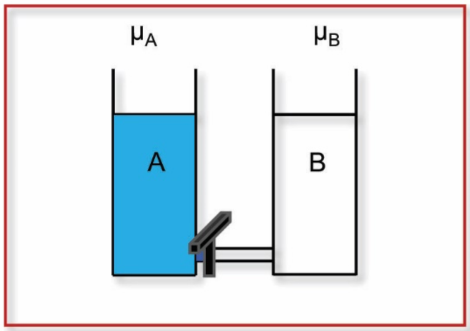


Figure 17.4 Container A (left) with a solution of higher concentration of a solute is brought in contact with another container B (right) that has a lower concentration of the same solute. Both are connected with a tube but separated with a stopcock. When the stopcock is open, the solute diffuses from the high-concentration region to the low-concentration region, spontaneously.

Let μ_A and μ_B be the chemical potentials of regions A and B above and let dn moles (> 0) of the substance move from region A to region B when the stopcock is opened. Region A loses dn moles and region B gains dn moles. The change in the free energy of the system dG is given by the following:

$$dG = \sum \mu_i \, dn_i = \mu_A \,(-dn) + \mu_B \, dn = (-\mu_A + \mu_B) \, dn$$

The first term in the sum has the negative sign for the mole numbers, because region A is losing the material, and the second term has a positive sign for change in mole numbers because region B is gaining these mole numbers.

For the flow of the spontaneous transfer of the substance from left to right, dG must be less than zero. Then, we can write the following:

$$(-\mu_A + \mu_B) \, dn < 0$$

Since dn cannot be less than 0, we conclude that the chemical potential of region B should be less than that of region B.

$$(-\mu_A + \mu_B) < 0$$

$$\mu_B < \mu_A$$

Therefore, we conclude that substances move spontaneously from a region of higher chemical potential to a region of lower chemical potential. The material transfer will continue till the chemical potentials of the two regions are the same, then dG = 0, and equilibrium is achieved.

$$\mu_B = \mu_A \; (equilibrium)$$

In summary, we showed that the chemical potentials of any two phases in equilibrium are equal and that substances are more uniformly distributed in the medium, spontaneously. Components move from high concentration regions to low concentration regions spontaneously until equilibrium is reached, which is the same way gases move from high-pressure to low-pressure regions, spontaneously.

17.2.4 Chemical potential of an ideal gas in a mixture of ideal gases

From the above, we recognize that when two phases are in equilibrium, their chemical potentials are equal. This condition is exploited to determine the chemical potential of an ideal gas in a mixture of ideal gases. For this purpose, we need to set up an experiment where the pure gas in a container is brought to equilibrium with a mixture of gases where it is one of the components in the mixture.

Consider pure hydrogen (left chamber) in a container separated by Pd membrane from pure nitrogen gas (right chamber) (Figure 17.5). Hydrogen dissolves spontaneously in the Pd metal and crosses over to the right side, but nitrogen does not dissolve in the Pd membrane and thus, cannot pass to the left chamber. Initially, the two gases are in their pure states, and as time progresses, some of the hydrogen gas dissolves in the Pd membrane forming a solid-gas solution. This happens spontaneously as the chemical potential of the hydrogen gas is lowered due to its dissolution in Pd and causes a reduction in the pressure of the pure hydrogen in the left chamber. The chemical potential of Pd is also lowered due to the formation of the solid-gas solution. Now, the hydrogen gas in the Pd membrane can escape into the nitrogen gas on the right side of the metal membrane, and this gas can occupy additional volume. This process continues until the chemical potential of the hydrogen gas mixed with the nitrogen gas is the same as that of the hydrogen on the left.

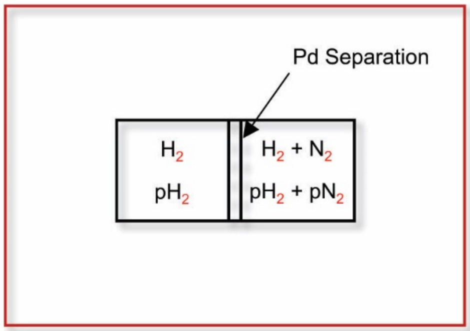


Figure 17.5 Pure hydrogen gas in equilibrium with a mixture of hydrogen and nitrogen separated by Pd membrane, which is permeable to hydrogen but not to nitrogen. The two hydrogen samples will have the same chemical potential at equilibrium.

The pressure of pure hydrogen decreases by this equilibration and the partial pressure of hydrogen in the mixture increases from zero to a certain value, proportional to its mole fraction in the mixture. When the system reaches equilibrium, the chemical potential of the pure hydrogen gas on the left equals that of the chemical potential of hydrogen in the mixture with nitrogen. Therefore, in the mixture, the chemical potential of pure hydrogen on the left equals the chemical potential of hydrogen on the right. Then we write the following:

$$\mu_{(hydrogen,\ mixture)} = \mu_{(hydrogen,\ pure)}$$

We write μ of pure hydrogen in terms of its value at one atmosphere and its pressure p.

$$\mu_{(\mathrm{hydrogen,\ pure})} = \mu^0_{(\mathrm{hydrogen,\ pure})} + \mathrm{R\,T} \ln \mathrm{p}$$

Then, we write the chemical potential of the hydrogen in the mixture in terms of the chemical potential of the pure hydrogen and its pressure($p_{hydrogen,pure}$), as following:

$$\mu_{(\mathrm{hydrogen,mixture})} = \mu^0_{(\mathrm{hydrogen,\ pure})} + \mathrm{R\,T} \ln \mathrm{p}_{(\mathrm{hydrogen,\ pure})}$$

At equilibrium, the pressure of pure hydrogen ($p_{hydrogen,\ pure}$) on the left side of the membrane should be the same as the partial pressure of hydrogen on the right side of the membrane ($p_{hydrogen,\ mixture}$), in the mixture. The partial pressure is then written in terms of mole fraction and total pressure of the mixture as follows:

$$\mathrm{p}_{(\mathrm{hydrogen,pure})} = \mathrm{p}_{(\mathrm{hydrogen,mix.})} = \mathrm{X}_{\mathrm{H_2}}\ \mathrm{p}_{\mathrm{total}}$$

The chemical potential of the hydrogen in the mixture is then written in terms of the chemical potential of hydrogen in the pure state, total pressure (p_{total}) of the gas mixture, and the mole fraction of hydrogen in the mixture as follows:

$$\mu_{H_2\,(mixture,T,p)} = \mu^0_{H_2\,(pure)} + R\,T \ln p_{total} + R\,T \ln X_{H_2}$$

One final adjustment is to recognize that the first two terms on the right can be replaced by the chemical potential of pure hydrogen when kept under the total pressure of the mixture.

$$\mu_{H_2\,(mixture,T,p)} = \mu_{H_2\,(pure,p_{total})} + R\,T \ln X_{H_2}$$

We immediately recognize that the second term on the right side is less than zero because the mole fraction of hydrogen is less than 1. Hence, the chemical potential of hydrogen in the mixture is less than that of pure hydrogen kept at the same pressure when a mixture is formed. Thus, the formation of a mixture of ideal gases is facilitated by a decrease in chemical potential.

For simplicity, we write μ* for the chemical potential of the pure substance I, while μ is used to denote that of the same component in the mixture.

$$\mu_i = \mu_i^* + R\,T \ln X_i$$

$$\mu^* = \mu_{pure}$$

We remind ourselves that μ_i and μ_i* are under the same pressure and total pressure and that the chemical potential of the mixture is less than the chemical potential of the pure substance. So, substances spontaneously mix naturally.

In summary, we showed that the chemical potential of an ideal gas in the mixture is less than that of its pure form, under the same p, T, and V conditions.

Example 17.4

Calculate Δμ of a gas component 1, when it is mixed with another in a 1 to 1 mol ratio at a total pressure of 5 atm and 300 K.

n=(1+1); n_1=1; n_2=1, x_1=(1/(1+1))=(1/2); T=300 K, and substituting in the equation below, we get the answer.

$$\Delta\mu_1 = RT\ln(X_i) = 8.3144\frac{J}{mol\ K}\ 300\ K\ ln\frac{1}{2} = -1.73\ kJ/mol$$

17.2.5 Chemical potential of mixing

We now use the above expression connecting the free energy of a component in a mixture with the free energy of the corresponding pure component and compute the free energy change when gases are mixed. This is different from the free energy of the mixture we discussed earlier. The chemical potential of mixing is required for our discussions of chemical reactions because reactions are always accompanied by mixing, either before (multiple reactants) or during the reaction (single reactant). Thus, the progress of the chemical reaction could have free energy decreases due to the chemical reaction as well as the ensuing mixing.

Consider several ideal gases of mole numbers n_1, n_2, n_3,… in a container separated from each other by walls, each component at pressure p and constant temperature (T) (Figure 17.6). By moving the walls, the gases mix spontaneously and equilibrate. We compute the change in the chemical potential of the system due to this mixing process while we assume that the gases are unreactive and that an ideal mixture is formed.

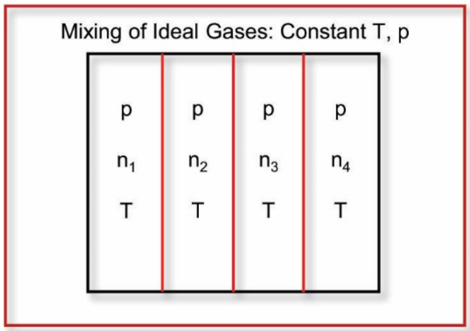


Figure 17.6 Mixing of several ideal gases separated by removable walls between them. Gibbs free energy change accompanying the spontaneous mixing is the free energy of mixing. Gases mix spontaneously with other gases, which is one of the fundamental properties of all gases.

The free energy of the initial state consisting of the pure gases separated by the walls is simply the sum of all the free energies. Each free energy term is the product of the number of moles of that component (n_i) and the chemical potential of the pure substance (μ*). Thus, we can write the following:

$$G\ (pure) = n_1\,\mu_1^* + n_2\,\mu_2^* + n_3\,\mu_3^* + \cdots = \sum \mu_i^*\,n_i$$

The G of the mixture on the other hand is given by the sum of the product of the mole numbers and their corresponding chemical potentials in the mixture (μ_i), which we worked out earlier.

$$(mixture) = \sum \mu_i\,n_i$$

The free energy of mixing (ΔG_{mix}) is equal to that of the mixture minus the sum of the free energies of the pure components as follows:

$$\Delta G_{mix} = \sum \mu_i\, n_i - \sum \mu_i^*\, n_i$$

Opening the sums and grouping the terms of the same components, we get a more compact sum.

$$\Delta G_{mix} = \sum n_i\,(\mu_i - \mu_i^*)$$

However, we already showed that the chemical potentials of the pure substance and that of the corresponding mixture are related as follows:

$$\mu_i = \mu_i^* + R\,T \ln X_i$$

Then, using the above, the mixing free energy is given by the following:

$$\Delta G_{mix} = \sum n_i\,(\mu_i^* + R\,T \ln X_i - \mu_i^*)$$

By canceling the equivalent terms with opposing signs and taking RT out of the sum, at constant T, we simplify the sum.

$$\Delta G_{mix} = R\,T \sum n_i \ln X_i$$

Recognizing that the mole fraction equals n_i/n, where n is the total mole numbers, we multiply and divide the sum with n and write the final expression for the mixing free energy.

$$\Delta G_{mix} = n\,R\,T \sum (n_i/n) \ln X_i$$

$$\Delta G_{mix} = n\,R\,T \sum X_i \ln X_i$$

Thus, the free energy of mixing depends on the mole fractions of each of the components of the mixture. A plot of this function for a two-component system is shown in Figure 17.7.

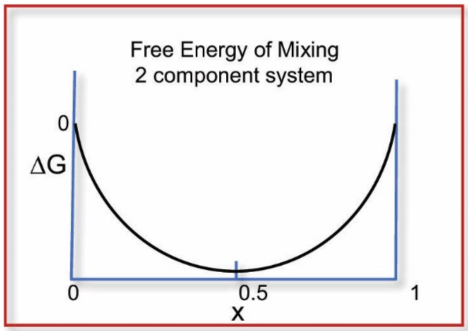


Figure 17. 7 Plot of the ΔG of mixing of two ideal gases (non-reactive) as a function of their mole fractions. When X =0 or when X =1, only pure components exist. Hence, mixing free energy is zero, the lowest value. When X = 0.5, the function has the minimum value <0.

The plot is an inverted bell-shaped curve. When the mole fraction is 1 or 0, only pure components exist and hence the mixing free energy is zero. When it is a 1:1 mixture, the mixing free energy has the lowest value.

Example 17.5

Calculate ΔG_{mixing} when two gases of 1 mol each are mixed at a pressure of 5 atm at 300 K.

n = (1+1); n_1 = 1; n_2 = 1, x_1 = (1/(1+1)) = (1/2); x_2 = (1/(1+1)) = (1/2); T = 300 K and substituting in the following, we get the answer.

$$\Delta G_{mixing} = nRT \sum x_i \ln x_i = 2\,mol * 8.3144 \frac{J}{mol\,K} * 300\,K\,[\frac{1}{2} * \ln\left(\frac{1}{2}\right) + \frac{1}{2} * \ln\left(\frac{1}{2}\right)] = 3.46\,kJ$$

In summary, the free energy of mixing ideal gases is less than zero and its value depends on the mole fractions of the components in the mixture. Since we computed the free energy of mixing, we can readily write entropy of mixing, enthalpy of mixing, and energy of mixing, and complete the discussion on mixing.

17.3 Entropy of Mixing

The entropy of mixing is important because the initial chemical reaction produces a mixture and there could be a substantial role for the entropy of mixing in driving the reaction, at least initially. Toward the end of the reaction, the entropy of mixing may be unfavorable because enriching the concentrations of the products in the reaction past halfway lowers entropy and a penalty will be applied. Thus, this topic is of importance not only for forming physical mixtures but also for chemical reactions. From the free energy of mixing, we can arrive at the entropy of mixing in two steps. We use the relation that connects G, T, and S to replace G.

$$\left(\frac{\partial G}{\partial T}\right)_{p,n_1,n_2,\ldots} = -S$$

Replacing G by ΔG and S by ΔS, we get the following:

$$\left(\frac{\partial \Delta G}{\partial T}\right)_{p,n_1,n_2,\ldots} = -\Delta S$$

We write corresponding equation for the mixture, as follows:

$$\Delta S_{mix} = -\left(\frac{\partial \Delta G_{mix}}{\partial T}\right)_{p,n_1,n_2,\ldots}$$

But, we know ΔG_{mix}, and find its derivative with T at constant p and mole numbers to continue.

$$\Delta S_{mix} = \frac{d}{dT}\left(-n\,R\,T\sum X_i \ln X_i\right)$$

$$\Delta S_{mix} = -n\,R\sum X_i\, ln\, X_i$$

The above expression shows that $\Delta S_{mix} > 0$ because n, R, and X are positive and the log of X_i is negative. The entire sum is negative therefore entropy of mixing is positive. A plot of ΔS_{mix} vs mole fraction for a two-component system is a bell-shaped curve (Figure 17.8), with the entropy of mixing being zero at X = 1 and x =0. At these points, we only have a pure component. When we have a 1:1 mixture, the entropy of mixing is maximized.

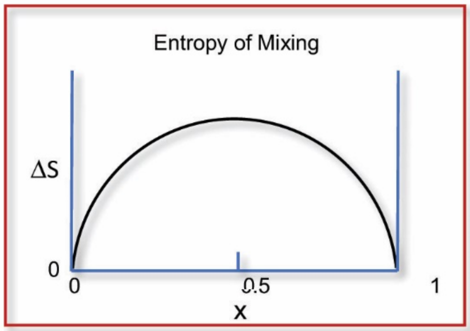


Figure 17. 8 Plot of ΔS of mixing of a two-component system (non-reactive) as a function of the mole fraction. When X =0 or when X =1, only pure components exist, and hence entropy of mixing is zero, the lowest value. When X = 0.5, the function has the maximum value.

In summary, we related the free energy of mixing with ΔS_{mix} and obtained the needed expression in a two-step derivation. The entropy of mixing is always greater than zero, and it has the highest value for a 1:1 binary mixture. Next, we will examine the enthalpy of mixing.

Example 17.6

What is the entropy of mixing when two gases of 1 mol each are mixed at 1 atm and 300 K?

n = (1+1); n_1 = 1; n_2 = 1, x_1 = (1/(1+1)) = (1/2); x_2 = (1/(1+1)) = (1/2) and substituting in the following, we get the answer.

$$\Delta S_{mixing} = nR \sum x_i \ln x_i = 2\, mol * 8.3144 \frac{J}{mol\, K} * \left[\frac{1}{2} * \ln\left(\frac{1}{2}\right) + \frac{1}{2} * \ln\left(\frac{1}{2}\right)\right] = 11.53\, J/K$$

17.4 Enthalpy of Mixing

Since we know ΔG$_{mix}$ and ΔS$_{mix}$, we can readily obtain ΔH$_{mix}$ using the fundamental thermodynamic relation as shown below.

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

Rearranging, we get ΔHmix and substituting, we get the following:

$$\Delta H_{mix} = \Delta G_{mix} + T\Delta S_{mix}$$

$$\Delta H_{mix} = n\, RT \sum X_i \, ln\, X_i - T\left(n\, R \sum X_i \, ln\, X_i\right) = 0$$

Thus, ΔH$_{mix}$ is 0 for ideal mixtures of ideal gases, and this is essentially because the ideal substances have no interactions among the particles. In other words, each gas molecule does not experience the presence of another gas molecule. A plot of ΔH$_{mix}$ vs mole fraction for a two-component system (Figure 17.9) is a flat line parallel to the X-axis.

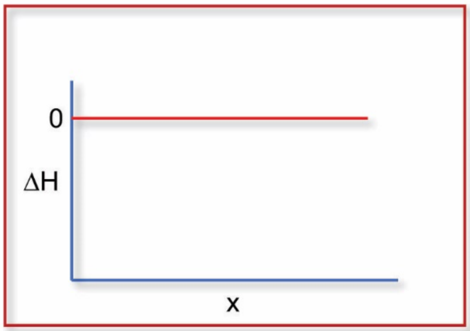


Figure 17. 9 Plot of the ΔH for the mixing of two non-reactive, ideal components as a function of the mole fraction. The enthalpy of mixing of ideal substances is zero since the particles have no interactions among themselves. This is an excellent criterion to decide if a mixture is ideal or not.

In summary, we have shown that the enthalpy of mixing of ideal gases is zero, using the expressions for the free energy of mixing and entropy of mixing. This is an important criterion to determine if a given mixture is ideal or not. One last remaining topic is the volume of mixing, discussed below.

Example 17.7

What is the enthalpy of mixing when oxygen and nitrogen are mixed in 1:1 mole ratio at 1 atm and 300 K, if both gases behave ideally?

For ideal gases, we get:

$$\Delta H_{mixing} = \Delta G_{mixing} T\Delta S_{mixing} = n\, RT \sum X_i \, ln\, X_i - T\left(n\, R \sum X_i \, ln\, X_i\right) = 0$$

17.5 Volume of Mixing

The volume of mixing at constant temperature is readily obtained by examining the relation between G, V, p, and T. We start with the fundamental equation, apply dT = 0, and write in terms of finite changes in free energy and volume.

$$dG = V\, dp - S\, dT$$

$$d\Delta G = \Delta V\, dp$$

We write the corresponding terms for the mixture and recognize the expression for the ΔG term as follows:

$$\Delta G_{mix} = n\, R\, T \sum X_i \ln X_i$$

Then, upon differentiation of free energy term with pressure, at constant T, gives the desired relation.

$$\Delta V_{mix} = \frac{d}{dp}(\Delta G_{mix})$$

$$\Delta V_{mix} = \frac{d}{dp}(n\,R\,T \sum X_i \ln X_i) = 0$$

Thus, the volume of mixing is zero for all values of the mole fraction, just like the enthalpy of mixing. Yet, another condition for the ideal behavior of the mixture is obtained.

$$\Delta V_{mix} = 0$$

In summary, we have deduced the volume of mixing to be zero for ideal gases by simply starting from one of the basic equations of thermodynamics and substituting for the free energy of mixing.

Example 17.8

What is the volume of mixing when hydrogen and helium are mixed in a 1:10 mole ratio at room temperature and atmospheric mixture, if the gases behave ideally?

Ideal gases mix with no change in volume, and we have ΔV_{mixing} =0.

$$\Delta V_{mix} = \left(\frac{d\Delta G_{mixing}}{dp}\right)_T = n\,R\,T \sum X_i \ln X_i = 0$$

17.6 Chemical Potential in Terms of Other Variables

We can write chemical potential as a function of Helmholtz free energy, enthalpy, or internal energy and these relations are useful for thermodynamic analysis of chemical systems. Chemical potential, for example, is defined in terms of Helmholtz free energy as a function of mole numbers as follows.

$$G = U + pV - T\,S = A + pV$$

$$dG = dA + d(pV)$$

Under constant T, V, and p conditions, we can write the following:

$$\mu_i = \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_{j\,\neq\,i}}$$

We also define chemical potential in terms of enthalpy. Since G = H – TS, at constant T, p, and V, conditions, we can write the following at constant S:

$$G = H - T\,S$$

$$dG = -SdT + Vdp$$

$$dG = dH - TdS$$

Under constant S conditions, we can define chemical potential as follows:

$$\mu_i = \left(\frac{\partial H}{\partial n_i}\right)_{S,p,n_{j\,\neq\,i}}$$

We write chemical potential as a function of the internal energy at constant T, and p as follows:

$$H = U + pV$$

$$\mu_i = \left(\frac{\partial(U + pV)}{\partial n_i}\right)$$

Under constant T, p, and V conditions, we get the desired expression.

$$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{T,p,V,n_{j\,\neq\,i}}$$

Chemical potential is related to the fundamental thermodynamic properties with the above restrictions, and the chemical potential is the underlying potential and kinetic energy changes that drive a process.

Example 17.9

What is the change in the internal energy of hydrogen when its mole numbers are increased from 3 to 3.5, in a mixture of hydrogen and helium, where the chemical potential of hydrogen is 25 J/mol, considering both gases as ideal?

$$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{T,p,V,n_{j \neq i}} \quad or \;\; \Delta n_i * \mu_i = \Delta U_i$$

So, substituting Δn_i=0.5 moles, μ_i = 25 J/mol, we get ΔU_i as 12.5 J.

17.7 Molecular Interpretation

Chemical potential successfully predicts the direction of a process under constant temperature and pressure conditions. Here, we connected it with mole numbers and gained insight into how ideal gases and real gases mix spontaneously. Mixtures of ideal gases are formed spontaneously and decrease the chemical potential of the system. Substances do not mix when the molecular interactions between one component and the other are not favorable. Unfavorable interactions raise the chemical potential and hence, it is not a spontaneous process.

The chemical potential is intimately related to the entropy and enthalpy changes occurring during a process and when molecular interactions are unfavorable, $\Delta H > 0$ while ΔS is still favorable for mixing. Thus, the interactions at the molecular level are responsible for macroscopic observations. Chemical potential is the total molar potential, and it is the ultimate thermodynamic property that drives chemical reactions or physical processes around us.

17.8 Applications in daily Life

Chemical potential is the foundation for our discussions of thermodynamics and its applications in real life as well as in practical applications of processes occurring in the world around us. Thus, when an apple falls from the tree, under constant p and T conditions, the chemical potential is decreasing, and the reverse process is not spontaneous because it raises the chemical potential of the system. Numerous spontaneous processes are around us, too many to cite here.

17.9 Key points

1. Chemical potential is the rate of change of Gibbs free energy and is equal to the molar free energy or the slope of the tangent of the function G(n).
$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_{j \neq i}}$$
2. The G of a mixture is simply the sum of the chemical potentials of the components in the mixture.
$$G_{mixture} = \sum \mu_i \, n_i$$
3. The chemical potential of an ideal gas increases with pressure, logarithmically.
$$\mu = \mu^\circ + RT \ln p_i$$
4. The chemical potential of a gas in a mixture of gases is less than the chemical potential of the corresponding pure component under the same conditions of pressure and temperature as the mixture.
$$\mu_i = \mu_i^* + RT \ln X_i$$
5. A gradient of concentration drives the uniform distribution of the material in solution, and at equilibrium, the chemical potential at any region A of the solution will be the same as at any other region B of the solution.
6. The free energy of mixing is dependent on the composition of the mixture and given by the following:
$$\Delta G_{mix} = n\,R\,T \sum X_i \ln X_i$$

7. The entropy of mixing is always positive and depends on the composition, as given by the following:
$$\Delta S_{mix} = -n\,R \sum X_i \ln X_i$$
8. The enthalpy of mixing and volume of mixing are zero for ideal mixtures due to the absence of any interactions between the gas particles. Thus, mixing is entirely driven by entropy changes and enthalpy changes do not contribute.
9. The change in internal energy of a component ΔU_i or ΔH_i in a mixture is related to its chemical potential μ_i and the change in its mole numbers n_i, at constant T, p, V, n_1, n_2….other than n_i.
$$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{T,p,V,n_{j\,\neq\,i}} \quad or \quad \mu_i = \left(\frac{\partial H}{\partial n_i}\right)_{S,p,n_{j\,\neq\,i}} \quad and \;\; \Delta n_i * \mu_i = \Delta U_i \;\; or \;\; \Delta n_i * \mu_i = \Delta H_i$$

17.10 Key terms and units

Chemical potential, Free energy of mixing, Enthalpy of mixing, Volume of mixing, and Entropy of mixing. The chemical potential has the units of energy per mole.

$$G_{mixture} = \sum \mu_i\, n_i$$

$$\mu = \mu^\circ + RT \ln p_i$$

$$\mu_i = \mu_i^* + RT \ln X_i$$

$$\Delta S_{mix} = -n\,R \sum X_i \ln X_i$$

$$\Delta G_{mix} = n\,R\,T \sum X_i \ln X_i$$

$$\Delta H_{mix} = n\,RT \sum X_i \ln X_i - T\left(n\,R \sum X_i \ln X_i\right) = 0$$

$$\Delta V_{mix} = \frac{d}{dp}(n\,R\,T \sum X_i \ln X_i) = 0$$

$$\mu_i = \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_{j\,\neq\,i}}$$

$$\mu_i = \left(\frac{\partial H}{\partial n_i}\right)_{S,p,n_{j\,\neq\,i}}$$

$$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{T,p,V,n_{j\,\neq\,i}}$$

17.11 Self Reflection

1. Imagine that your dorm room is a system filled with water. If one mole of sugar is dissolved in that water, what is the name given for the change in the Gibbs free energy of the system? Justify your response.
2. Consider the preparation of morning coffee at your home. Discuss mixing free energy, the entropy of mixing, and enthalpy of mixing when you add sugar and creamer to the black coffee.
3. Explain to your younger sibling, using lay terms, how free energy drives the mixing of milk and water but not oil and water.
4. You plan to develop a startup company to make new batteries. To assess the feasibility of the proposed battery chemistry, would you calculate the change in Gibbs free energy of reagents or Helmholtz free energy of reagents as the reaction gives rise to products? Why?
5. Plot μ vs n, μ vs T, μ vs p and μ vs V for a spontaneous process and choose appropriate conditions.

17.12 Further Reading

1. https://ocw.mit.edu/courses/materials-science-and-engineering/3-00-thermodynamics-of-materials-fall-2002/lecture-notes/lecture_20_oneside.PDF

2. https://ocw.mit.edu/courses/chemistry/5-60-thermodynamics-kinetics-spring-2008/video-lectures/lecture-14-multicomponent-systems-chemical-potential/
3. https://chem.libretexts.org/Textbook_Maps/Physical_and_Theoretical_Chemistry_Textbook_Maps/Book%3A_Physical_Chemistry_(Fleming)/7%3A_Mixtures_and_Solutions/7.3%3A_Chemical_Potential

17.13 Self Tests

1. The mole numbers of components in a reaction mixture change when

   a. reactions proceed

   b. equilibrium is achieved

   c. substances are added or removed

   d. both a and c

   e. none of these

2. Balanced chemical equations show certain mole numbers of pure reactants react

   a. completely to form pure products

   b. to form products

   c. to form pure products but some reactants may remain

   d. to form mixtures of products and reactants

   e. none of these

3. The Gibbs free energy of the reaction is

   a. the sum of the Gibbs free energies of the pure reactants subtracted from the sum of Gibbs free energies of pure products

   b. the Gibbs free energies of the reactants minus Gibbs free energies of the products

   c. the sum of the Gibbs free energies of the pure reactants subtracted from Gibbs free energy of the mixture of products

   d. the sum of the Gibbs free energies of the pure reactants and Gibbs free energies of pure products

   e. none of these

4. A mixture is often formed during a chemical reaction only when

   a. the reaction involves multiple reactants and products

   b. the reaction involves only one reactant

   c. the reaction involves only one product

   d. there are multiple reactants and products

   e. none of these

5. A fundamental process common to all chemical reactions at the beginning is

   a. boiling

   b. melting

   c. sublimation

   d. the formation of a mixture

   e. none of these

6. The chemical potential of a substance is

a. its total energy content

b. its total Gibbs free energy

c. its molar Gibbs free energy

d. its molar enthalpy

e. none of these

7. The rate of change of Gibbs free energy with respect to mole number is

a. enthalpy

b. molar entropy divided by enthalpy

c. chemical potential

d. physical potential

e. none of these

8.The rate of change in G with mole number i at constant T, p, and other mole numbers of a component in a mixture of j components is

a. $\left(\frac{\partial G}{\partial n_i}\right)_{p,n_1,\ldots except\ n_i}$

b. $\left(\frac{\partial G}{\partial n_i}\right)_{T,n_1,\ldots except\ n_i}$

c. $\left(\frac{\partial G}{\partial n_j}\right)_{T,p,n_1,\ldots except\ n_i}$

d. $\left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_1,\ldots except\ n_i}$

e. none of these

9.The exact differential of G with respect to T, p, and mole numbers (n_1, n_2, n_3,…n_i) is

a. $dG = \left(\frac{\partial G}{\partial n_1}\right)_{p,n_2,\ldots} dn_1 - \left(\frac{\partial G}{\partial n_2}\right)_{T,p,n_1,\ldots} dn_2 - \cdots ..$

b. $dG = \left(\frac{\partial G}{\partial n_1}\right)_{n_2,\ldots} + \left(\frac{\partial G}{\partial n_2}\right)_{T,p,n_1,\ldots} + \cdots$

c. $dG = \left(\frac{\partial G}{\partial n_1}\right)_{T,p,n_2,\ldots} dn_2 + \left(\frac{\partial G}{\partial n_2}\right)_{T,p,n_1,\ldots} dn_3 \ldots$

d. $dG = \left(\frac{\partial G}{\partial n_1}\right)_{T,p,n_2,\ldots} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{T,p,n_1,\ldots} dn_2 \ldots$

e. none of these

10. The change in the Gibbs free energy of a mixture with change in composition of the mole numbers (n_i) and their chemical potentials (μ_i) is

a. $dG = -(\mu_1\, dn_1 + \mu_2\, dn_2 + \mu_3\, dn_3 \ldots$

b. $dG = \mu_1\, dn_1 - \mu_2\, dn_2 - \mu_3\, dn_3 \ldots$

c. $dG = \mu_1\, dn_1 + \mu_2\, dn_2 + \mu_3\, dn_3 \ldots$

d. $dG = -\sum \mu_i\, dn_i$

e. none of these

11. Plot of G vs n for a pure component has a slope equal to

a. enthalpy

b. entropy

c. chemical potential

d. Gibbs free energy

e. none of these

12. The Gibbs free energy of a mixture in terms of the chemical potentials (μ_i) and their mole numbers (n_i) is

a. $\int \sum \mu_i \, dn_i$

b. $\sum \mu_i \, n_i$

c. $-\int \sum \mu_i \, dn_i$

d. both a and b

e. none of these

13. The chemical potential (μ) of a gas at any pressure p is related to its chemical potential at 1 atm (μ°) as

a. $\mu = \mu^0 + R\,T \ln p$

b. $\mu = \mu^0 + \ln p$

c. $\mu = \mu^0 - R\,T \ln p$

d. both a and b

e. none of these

14. Plot of chemical potential vs pressure of an ideal is

a. linear with a slope equal to T

b. linear with a slope equal to R

c. linear with a slope equal to pV

d. linear with a slope equal to -RT

e. none of these

15. The chemical potential of a substance is μ_A at region A and μ_B in another region B and the substance diffuses spontaneously from region A to region B, if

a. $\mu_A = \mu_B$

b. $\mu_A > \mu_B$

c. $\mu_A < \mu_B$

d. $\mu_A / \mu_B = 1$

e. none of these

16. The chemical potential (μ_i) of the ith component having a mole fraction X_i in a mixture is related to its chemical potential in the pure state (μ_i^*) as

a. $\mu_0 = \mu_i^* + R\,T \ln X_i$

b. $\mu_x = \mu_i^* + R\,T \ln X_i$

c. $\mu_n = \mu_i^* + R\,T \ln X_i$

d. $\mu_i = \mu_i^* + R\,T \ln X_i$

e. none of these

17. The change in the Gibbs free energy due to mixing in terms of total mole numbers (n) in the mixture, temperature (T), gas constant (R), and the mole fraction of the ith component (X_i) is

    a. $n\,R\,T\,\sum \ln X_i$

    b. $n\,/R\,T\,\sum X_i \ln X_i$

    c. $-n\,R\,T\,\sum X_i \ln X_i$

    d. $n\,R\,T\,\sum X_i \ln X_i$

    e. none of these

18. The entropy of mixing of a binary mixture is

    a. maximum at 1:1 mole ratio of the two components

    b. minimum at 1:1 mole ratio of the two components

    c. zero at all compositions

    d. can't say

    e. none of these

19. The enthalpy as well as the volume of mixing for an ideal mixture is

    a. >1

    b. <1

    c. =0

    d. = infinity

    e. none of these

20. The change in the chemical potential when a gas of 1 mol expands from 5 atm to 1 atm at 300 K is

    a. -3861.6

    b. -3861.6 J/mol

    c. 3861.6 J/mol

    d. -3861.6 J/K

    e. none of these

17.14 Self Tests Key

1. d, 2. a, 3. a, 4. e, 5. d, 6. c, 7. c, 8. d, 9. d, 10. e, 11. d, 12. d, 13. a, 14. c, 15. b, 16. d, 17. d, 18. a, 19. c, 20.b

17.15 Problems

1. The change in the chemical potential when a gas of 1 mol expands from 5 atm to 1 atm at 300 K is (Ans. -3861.6 J/mol)
2. What is the change in the enthalpy of oxygen dissolved in water, if it behaves as ideal gas, when its mole numbers are increased by 0.1 mol under constant entropy, temperature, and volume, if its initial chemical potential in the mixture to start with is -16.4 kJ/mol? (Ans. -1.64 kJ/mol)
3. What is the entropy of mixing of pure oxygen and pure nitrogen under ambient conditions to produce air composition? (mole fraction of oxygen in air is 0.16) (Ans. 128.1 J/K kg)
4. What is the mixing free energy when 1 kg of air is produced by mixing 18% oxygen and 82% nitrogen, under ambient conditions? (Ans. -384 kJ/kg)
5. Chemical potential of pure oxygen is zero under ambient conditions, what is its chemical potential in the air which contains roughly 18% oxygen? (Ans. -4.55 kJ/mol)

6. The atmospheric pressure on mount Everest is roughly a third of the pressure at sea level. What is the chemical potential of oxygen on the mountain in the in-breath at about 310 K, even if its mole fraction is 1 in oxygen supplemental packs? (Ans. -2.8 kJ/mol)
7. The chemical potential of oxygen in the tissues is nearly half of that in air. Explain why hypoxia sets in quickly when you are on a mountain top that is around 8 miles high?
8. Air travel made it possible to travel long distances in short times but the high altitude travel has its own issues to address. When a plane is traveling at a cruising height of 30,000 feet, oxygen partial pressure drops from 150 Torr at sea level to about 30 Torr at this height. What is the change in the chemical potential of oxygen if the cabin is at 300 K but not pressurized? (Ans. -4.01 kJ/mol)
9. The mole fraction of a gas in a mixture of gases (ideal) is changed by 10% of its initial value at constant temperature and volume. What is the change in its Helmholtz free energy? (Ans. 10.13 J)
10. Explain based on chemical potential why do some substances mix spontaneously? Also explain who do other substances do not mix at all?

Chapter 18. Gibbs Free Energy and Equilibrium

After completing this chapter, you will be able to:

- Recognize two different contributions of Gibbs free energy toward the progress of a chemical reaction.
- Relate the Gibbs free energy change to the equilibrium constant.
- Use Gibbs free energy to control the composition of the chemical equilibrium.

Goals

- Synthesize an equation relating the Gibbs free energy and the progress of the chemical reaction.
- Connect the mixing free energy and the reaction free energy with the reaction progress.
- Deduce the relation between the equilibrium constant and equilibrium pressures.
- Quantify the effect of temperature, pressure, and concentrations on chemical equilibrium.

18.1 Why Study this?

The study of chemistry requires the study of chemical reactions, inevitably. Reaction free energy ($\Delta G_{reaction}$) is of importance to predict if a given chemical reaction will move forward, if it is in equilibrium, or if it will move in the reverse direction. This aspect is of paramount importance for our investigation of why chemical reactions occur. A more detailed understanding of the free energy transactions of a chemical reaction will provide better clues and handles for controlling the chemical reactions, the main task of a chemist. Chemical potential, in this context, provides a practical means to control the position of equilibrium as well as the direction of a chemical reaction. Thus, this chapter is a milestone in our discussion of the thermodynamics of chemical reactions.

We recognize that many chemical reactions are of importance in our daily lives, in the body, in the environment, and industry. Thermodynamic control over them is a convenience for improving our productivity while caring for the environment. Many biochemical reactions taking place in our bodies are controlled by the same principles and hence are of immense importance in health and well-being. Chemical reactions are utilized for the manufacturing of most industrial goods, pharmaceuticals, agrochemicals, and food. Thus, the role of chemical potential in controlling these chemical reactions, as well as the equilibria, are of immediate concern to us and worthy of study.

18.2 Free Energy of a Chemical Reaction

We looked at the free energy of a mixture and the free energy of mixing, in the previous chapter, and this is of significance in the discussions of controlling a chemical reaction as well. For example, even if we start with a single reactant for our reaction, a mixture is created when the chemical reaction begins. That is, a small amount of product formed, even at the beginning of the reaction, creates a mixture of the reactant and the product. As the reaction progresses, a mixture of reactants and products continues to form until the reaction is complete. Only when the reaction is 100% complete and all reactants are consumed giving rise to only one product will we achieve a pure product. Under all other conditions, we end up with a mixture, and hence mixing parallels the chemical reaction. If we start with multiple reactants, then we need to mix them before the reaction can commence. Therefore, ΔG_{mixing} contributes to the reaction free energy of any reaction, not only at the beginning but also throughout the reaction course. This is a powerful recognition because this insight provides another handle to control the progress of a chemical reaction. However, the mixing free energy is negative for all ideal gases, but the mixing enthalpy and mixing volume are zero. The increase in entropy, due to the mixing of the ideal gases, drives the spontaneous formation of a mixture, and mixture formation is a pre-requisite for chemical reactions that involve more than one reagent.

The criterion that we obtained for a chemical reaction to proceed forward under constant T and p conditions is $\Delta G < 0$; or $\Delta G > 0$ to proceed in the reverse direction; or $\Delta G = 0$ for achieving equilibrium. We ask the question, how does the free energy of the system change, as the chemical reaction progresses? We keep in mind that this is likely to involve the reaction free energy as well as the mixing free energy.

The reaction progress is zero when we have only pure reactants. The very next thing is the mixing of the reactants for the reaction to occur. This itself lowers the free energy of the system because the mixing of ideal gases is a spontaneous process. As the reaction kicks in, products are created. When a small amount of product or products are produced, the Gibbs free energy decreases further because of the mixing of newly produced products with existing reaction mixture (ΔG_{mixing}), but there is also the contribution of the free energy change due to the chemical reaction as well ($\Delta G_{reaction}$). Thus, the total change in G is the sum of mixing free energy and the reaction free energy.

$$\Delta G = \Delta G_{reaction} + \Delta G_{mixing}$$

At the very end of the chemical reaction, when the progress is complete, the reactants are completely consumed while the products are fully produced, but this does not happen often. Normally, a mixture is obtained in our reaction vessel, and products are not in their pure states unless the reaction gives only one product, and all reactants are completely consumed. Most reactions do not go to completion even when stoichiometric amounts of the reactants are used. Even when the reaction is 100% complete and reactants are chosen in their corresponding stoichiometric amounts, there is still the possibility that the reaction generates more than one product. Then, we still have a mixture. If one of the reagents is in excess, then we will certainly have a mixture in the end, even if the reaction is complete and gives only one product. Thus, most chemical reactions fall under the category that a mixture is produced at the end of the day, with very few exceptions. Therefore, in general, we consider two separate contributions to the chemical reaction: reaction free energy and mixing free energy. We need to look at both parameters to examine the chemical reaction and its progress.

18.2.1 Stoichiometric coefficients and the reaction free energy

Consider a chemical reaction where the reactants A and B produce products C and D with their corresponding stoichiometric coefficients, ν_I, as defined by the chemical reaction below.

$$\nu_A\, A + \nu_B\, B \rightarrow \nu_c\, C + \nu_D\, D$$

The stoichiometric coefficient of A is ν_A, that of B is ν_B, and so on. As the chemical reaction progresses, A and B will be consumed in proportion to their stoichiometric coefficients, and C and D are produced in proportions of their respective stoichiometric coefficients. The above chemical reaction describes the following scenario. Initially, when the reaction progress is zero, we have only pure reactants and no products. And at the end, when the reaction progress is 100% complete, we have only pure products, no leftover reactants, and all substances are in their pure states, not as mixtures. Thus, the free energy change is between the initial state of pure reactants and the final state is that of the products in their pure state. When we write a reaction in the above manner, we imply that pure reactants give rise to pure products, with 100% conversion of reactants to products in finite proportions to the corresponding pure products.

We assign a negative sign to the stoichiometry coefficient of reactants because their mole numbers diminish with reaction progress. The stoichiometric coefficients of the products, in contrast, are given a positive sign because their mole numbers increase as the reaction progresses. Thus, we write the corresponding mathematical equation representing the above chemical reaction as the following:

$$-\nu_A\, A - \nu_B\, B + \nu_c\, C + \nu_D\, D = 0$$

We write a general equation involving i components for the chemical reaction as follows, where the stoichiometric coefficient of the ith component is νi of the chemical component AI.

$$\sum \nu_i\, A_i = 0$$

Example 18.1

Calculate the sum of the stoichiometric coefficients of the reaction between hydrogen and oxygen, considering their ideal behavior to produce water vapor at 5 atm and 300 K by a catalyst.

$$2H_2 + O_2 \rightarrow 2H_2O$$

$$\sum \nu_i = 2 - 1 - 2 = -1$$

18.2.2 Exoergonic, endergonic and Isoergonic reactions

We divide our discussion of reactions into three cases: those that are exergonic (ΔG <0, Figure 18.1), isoergonic (ΔG =0, not shown), and endergonic (ΔG >0, Figure 18.2).

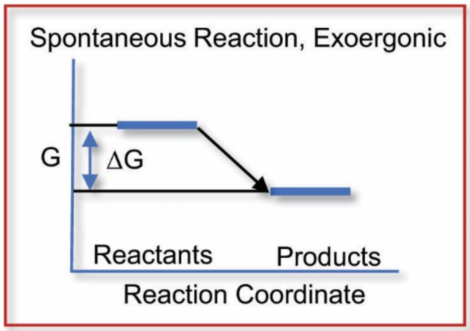


Figure 18.1 Gibbs free energy changes of the system when ΔG <0, exergonic, the process is spontaneous and the reaction progresses forward converting pure reactants to the corresponding pure products. Energy changes due to mixing are not included.

The change in Gibbs free energy of the exoergonic reaction is negative, meaning that the products are more stable than the reactants. Thus, the reaction progresses in the forward direction to minimize the Gibbs free energy of the system, not internal energy, or enthalpy. Thus, chemical reactions spontaneously occur to minimize the Gibbs free energy of the system and produce more stable products. When G does not decrease any more or ΔG = 0, then the system is at equilibrium. The sum of Gibbs free energies of the reactants is exactly equal to the sum of the Gibbs free energies of the products, and the system reaches the lowest Gibbs free energy state. No more changes will occur under these conditions, and we say that the system has attained equilibrium.

Similarly, the reverse reaction occurs when the reactants are more stable than the products or have lower free energy than the products, and the system moves spontaneously in the reverse direction to minimize the Gibbs free energy (Figure 18.2). When the Gibbs free energy is minimized this way, the system reaches chemical equilibrium.

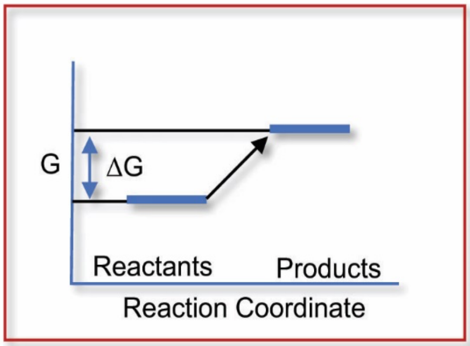


Figure 18.2 Gibbs free energy changes of the system when ΔG >0, endergonic, the reverse process is spontaneous and the reaction progresses backwards spontaneously, converting pure products to pure reactants. Energy changes due to mixing are not included.

At equilibrium, we recognize that the reactants continue to form products and products continue to form reactants, but the progress of the two reactions are exactly matched such that net change in the Gibbs free energy is zero.

Example 18.2

Calculate the change in chemical potential when pure oxygen and hydrogen react to give pure water vapor at 300 K, 1 atm. ($\mu_{\text{water vapor, 300 K, 1 atm}}$= -228 kJ/mol)

$$\Delta\mu = \mu_{products} - \mu_{reactants} = -228\,\frac{kJ}{mol} - 0\,\frac{kJ}{mol} - 0\,\frac{kJ}{mol} = -228\,\frac{kJ}{mol}$$

18.3 G and Reaction Progress

The change in the Gibbs free energy of the system during a reaction is simply equal to the sum of the chemical potentials of the reactants and products (μ_i) multiplied by the changes in their respective mole numbers (dn_i). For a generic reaction consisting of i reaction components (see above), where μ_i is the ith chemical component and ν_i is its stoichiometric coefficient, we can write the corresponding change in G as follows:

$$dG = \sum \mu_i \, dn_i$$

We recognize that we have used the chemical potentials of the substances as they are in the mixture, not in their pure states. Hence, intrinsically, we included the mixing free energy into the Gibbs free energy of the reaction. We also recognize that dG is changing as the reaction is progressing, or dn_i is changing, because the composition of the system changes as the reaction progresses.

Since dG is a function of the reaction progress, we first define reaction progress. The progress of a chemical reaction (ξ) is defined to be zero at the beginning of the reaction and equals 1 when the reaction is complete. Then, when the reaction is halfway done, ξ =0.5.

ξ = 0 at the beginning of the reaction

ξ = 1 when the reaction is complete

Now, we will connect the change in ξ with dG and then connect it with the reaction free energy. Let n°_i be the number of moles of the ith substance at the beginning of the reaction and let n_i be the mole numbers of the ith component at any time when the reaction progress is ξ. As the reaction progresses, $\nu_I \, \xi$ moles of the reactant i are consumed, and the mole numbers (n_I) at this degree of progress is given as follows:

$$n_i = n_i^0 + \nu_i \, \xi$$

We remind ourselves that the stoichiometric coefficients of the reactants are negative and those of the products are positive. By differentiating the above expression, we get the infinitesimal change in the mole numbers as a function of the infinitesimal change in the reaction progress as follows, which can be readily related to dG of the reaction.

$$dn_i = 0 + \nu_i \, d\xi$$

The initial mole numbers that we choose are fixed at some value and thus independent of the reaction progress and its differential drops off. We also recognize that the stoichiometric coefficients are independent of the reaction progress, and hence not variables in our equation. We write dG of the reaction mixture from the above discussions and replace dn_i with the $d\xi$ term as follows:

$$dG = \sum \nu_i \, \mu_i \, d\xi$$

Therefore, the rate of change of Gibbs free energy with reaction progress is given by the sum of the chemical potentials of the reactants and products as shown below.

$$\frac{dG}{d\xi} = \sum \nu_i \, \mu_i$$

A plot of G vs ξ would give us a function that will have a slope of its tangent defined by the chemical potentials of the reactants and products, as the reaction composition is changing (Figure 18.3). The total Gibbs free energy is chosen to be greater than the total Gibbs free energy of the products or the reaction is exergonic.

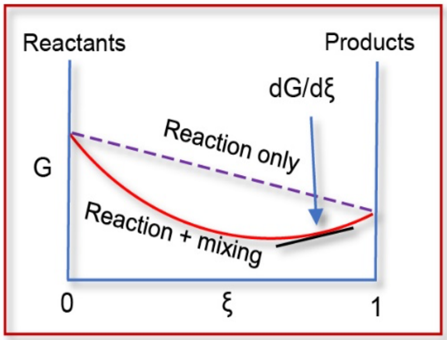


Figure 18.3 Plot of the Gibbs free energy of the reaction mixture of a two-component system as a function of the reaction progress for an exergonic reaction.

Example 18.3

When the reaction is about to begin (ξ =0), G is the sum of the Gibbs free energies of the pure reactants. When the progress is complete (ξ =1), it is the sum of the Gibbs free energy of the pure product. At all other compositions, G is the sum of the Gibbs free energies of the product and reactant in their corresponding mixtures (blue). The linear plot represents the contribution to G due to the chemical reaction (purple), while the blue concave curve represents the sum of the free energy due to the mixing of the product with the reactant as well as the chemical reaction.

Initially, when the reaction is about to start, ξ = 0 and G is the total Gibbs free energy of the pure reactants. As the reaction progresses, dG <0 (red curve) because the sum of the Gibbs free energies of the products is less than those of the reactants (exergonic) and decrease in G also has the contributions of ΔG_{mixing}. The red curve represents the sum of the reaction free energy and the mixing free energy, while the dashed line corresponds to the changes in G due to the chemical reaction only. Free energy changes due to mixing are not included. When the reaction moves forward, dG<0 as some reactants are converted to products of lower free energy. The plot has a negative slope or dG/dξ <0 and thus dξ >0 meaning that the reaction progresses in the forward direction.

Due to the mixing of the reactants with the products, the blue curve is lower than the linear plot, at any given point, other than when ξ =0 or 1. As the plot shows, the slope of the curve decreases as the reaction progresses and dG/dξ =0 at some point before the end of the reaction. As this composition and reaction progress, equilibrium is achieved, and further progress will not take place. This is because, at progress greater than the equilibrium point, the slope of the red curve is positive and dG >0 to the right of this point. The forward reaction is no longer spontaneous. Thus, even when the reaction overall is favorable, there could be certain amounts of reactants that will be leftover due to the presence of the equilibrium point before the completion of the reaction. Theoretically speaking, it is almost impossible to get 100% yield for a chemical reaction, at least from these rudimentary arguments. In the next section, we separate mixing free energy from the reaction free energy.

18.4 Relation between ΔG_{mixing} and $\Delta G_{reaction}$

The G of the reaction mixture is given by the following, where the reaction is treated as a mixture. This is just the free energy of the mixture, as derived in the previous chapter.

$$G\ (total) = \sum n_i\, \mu_i$$

But to get the reaction free energy, we need to introduce the chemical potentials of the pure reactants and pure products and account for the mole numbers of the reactants and the products. We represent these as μ_i^* where the star indicates that the substance is in its pure form. We add and subtract the chemical potentials of the pure substances on the right of the above equation.

$$G\ (total) = \sum n_i\,(\mu_i - \mu_i^* + \mu_i^*) = \sum n_i\,(\mu_i - \mu_i^*) + \sum n_i\, \mu_i^*$$

We recognize that the first sum on the right is the difference in the free energy of the pure components and the components in the mixture. The second sum is that of the free energies of all the pure components. It represents the reaction free energy as the pure reactants produce only pure products. So, we replace the two sums with these corresponding terms to get the following equation:

$$G\,(total) \;=\; \Delta G_{mixing} + \; G_{pure\ substances}$$

Differentiating the above with respect to the reaction progress, on both sides, we get the following:

$$(dG/d\xi) = d\big(\Delta G_{mixing}\big)/d\xi + d\big(G_{pure\ substances}\big)/d\xi$$

Thus, the slope of the plot of G (total) vs ξ or dG/dξ is the sum of the derivatives of ΔG_{mixing} and $G_{reaction}$ with respect to the reaction progress.

18.4.1 Endergonic reactions

Now, we can consider endergonic reactions and ask, will it be possible for these reactions to occur? Since the ΔG >0, we would predict that the reaction should not proceed. But a closer examination of the plot of G vs reaction progress (Figure 18.4) reveals that the reaction could be driven, at least to some extent, by the Gibbs free energy of mixing.

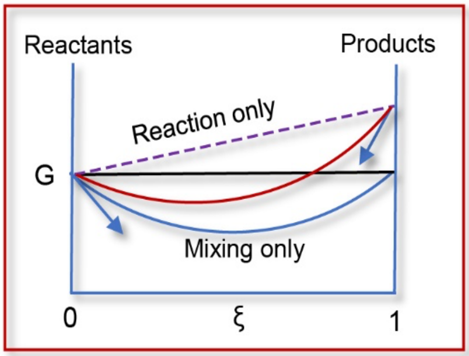


Figure 18.4 Plot of the Gibbs free energy of the reaction mixture of a two-component system (red curve) as a function of the reaction progress for an endergonic reaction.

When the reaction is about to begin (ξ =0), G is the Gibbs free energy of the pure reactant and when the progress is complete (ξ =1), it is the Gibbs free energy of the pure product. At all other compositions, G is the sum of the Gibbs free energies of the product and reactant in their corresponding mixtures. The linear plot represents the contribution to G from the chemical reaction (purple dashed line), while the concave curve (blue) represents a favorable contribution of the mixing of the product with the reactant to the total G of the reaction (red curve).

The plot of G vs ξ for the endergonic reaction (Figure 18.4) for a two-component system has pure reactant on the left Y-axis and pure product on the right Y-axis. At any point in between, Gibbs free energy of the reaction is the sum of the free energies of the pure reactant producing the pure product (purple dashed line) at that composition. When the reaction proceeds by an infinitesimal amount, a mixture is produced (blue line), and the reaction mixture will have lower free energy than the corresponding pure components (red curve).

The reaction could proceed, initially, and this is because the slope of the red curve at ξ =0 is <0. As the reaction progresses, the system reaches equilibrium, dG = 0, and any further change in composition only raises the Gibbs free energy, and hence is not spontaneous but the reverse reaction is. Thus, the mixing free energy can drive the reaction forward, even if the reaction is endergonic to some degree. The equilibrium point depends on the slope of the purple dashed line, which in turn depends on the depth of the blue curve. Finally, we recognize that endergonic reactions can also occur, even to a small extent, and reach equilibrium, and no reaction can be 100% unreactive, at least theoretically.

Example 18.4

Calculate the mixing free energy and the reaction free energy when two gases of 1 mol each (chemical potentials 1 kJ/mol and 1.5 kJ/mol) react to give a product (chemical potential 1 kJ/mol) with stoichiometric coefficients -1, -1, and +1, respectively, halfway to completion at 5 atm and 300 K.

We use the expressions: $\Delta G_{reaction} = \sum n_i \, \mu_i \; and \; \Delta G_{mixing} = n\,R\,T \sum x_i \ln x_i$

Consider the reaction -1 Reactant$_1$ – 1 Reactant$_2$ + 1 Product$_1$ = 0; at 50% completion, we have:

$$\Delta G_{reaction} = \sum n_i \, \mu_i = 0.5\,mol\left(1\frac{kJ}{mol}\right) - 0.5\,mol\left(1\frac{kJ}{mol}\right) - 0.5\,mol\left(1.5\frac{kJ}{mol}\right) = -0.75\,kJ$$

$$\Delta G_{mixing} = n\,R\,T \sum x_i \ln x_i = 1.5\,mol * 8.3144\frac{J}{K\,mol} * \ 300\text{ K}\left[\frac{0.5}{1.5}\ln\left(\frac{0.5}{1.5}\right) + \frac{0.5}{1.5}\ln\left(\frac{0.5}{1.5}\right) + \frac{0.5}{1.5}\ln\left(\frac{0.5}{1.5}\right)\right]$$

= -4.11 kJ

18.5 Gibbs Free Energy and the Equilibrium Constant

From the above discussions, one would expect that the Gibbs free energy of the reaction is related to the equilibrium constant. The position of equilibrium, for example, depends on the slopes of the plots of the reaction free energy of the pure reactants and their free energy of mixing. The following provides an important insight into this relationship.

18.5.1 Chemical potential and chemical equilibrium

Consider a reaction where all the reactants and products are ideal gases, and we assume that these ideal gases do react to produce products but otherwise have no interactions. The Gibbs free energy of the reaction is simply the difference in the Gibbs free energies of the products and the reactants as follows:

$$\Delta G_{reaction} = \sum G_{products} - G_{reactants}$$

The above free energy term accounts for the reaction free energy as well as the mixing free energy. We will attempt to separate them by writing chemical potentials with the respective stoichiometric coefficients as follows:

$$\Delta G_{reaction} = \sum \nu_i \, \mu_i$$

The chemical potentials of the components in the mixture (μ_i) are now replaced with those of the corresponding pure substances (μ_i*) under pressure p$_i$ using the relation $\mu_i = \mu_i^* + R\,T \ln p_i$, we get:

$$\Delta G_{reaction} = \sum \nu_i \,(\mu_i^* + R\,T \ln p_i)$$

Rearranging the terms by grouping, we get those of the pure reactants and products separated as follows:

$$\Delta G_{reaction} = \sum \nu_i \, \mu_i^* + \sum \nu_i \, R\,T\,ln\,p_i$$

Recognizing that the first sum on the right is the sum of the free energies of pure reactants and pure products, we replace it with the symbol ΔG˚ as defined below.

$$\Delta G^0 = \sum \nu_i \,(\mu_i^*)$$

Therefore, the total free energy of the reaction is written as follows:

$$\Delta G_{reaction} = \Delta G^0 + R\,T \sum \nu_i \ln p_i$$

Example 18.5

Calculate ΔG reaction when two ideal gases of 1 mol each with a partial pressure of 1 atm each, react halfway as follows, at 300 K. (μ_A = 1 kJ/mol; μ_B = 4.5 kJ/mol; μ_C = 1 kJ/mol at 300 K, 5 atm)

$$1\,A + 1\,B \rightarrow 2\,C$$

$\Delta G^0 = G_{products} - G_{reactants}$

$$= \left(1\frac{\mathrm{kJ}}{\mathrm{mol}}\right) * (2) - \left(1\frac{\mathrm{kJ}}{\mathrm{mol}}\right) * (1) - \left(0.4458\frac{\mathrm{kJ}}{\mathrm{mol}}\right) * (1) = -3.45\frac{\mathrm{kJ}}{\mathrm{mol}}$$

$$R\,T\sum \nu_i \ln p_i = 8.3144\frac{J}{K\,mol} * 300\,K\left[2 * \ln\left(1\frac{atm}{atm}\right) - 1 * \ln\left(0.5\frac{atm}{atm}\right) - 1 * \ln\left(0.5\frac{atm}{atm}\right)\right] = 3.46\frac{kJ}{mol}$$

$$\Delta G_{reaction} = \Delta G^0 + R\,T\sum \nu_i \ln p_i = -42\,J/mol$$

18.5.2 Equilibrium constant and ΔG˚

At equilibrium, we note that ΔG = 0 for the reaction, and we use the equilibrium pressures to obtain the equilibrium constant, next.

$$\Delta G_{reaction} = 0 = \left(\Delta G^0 + R\,T\sum \nu_i\, ln\, p_i\right)$$

We write ΔG˚ in terms of the partial pressures of reactants and products at equilibrium as follows:

$$\Delta G^0 = -R\,T\sum \nu_i\,(\ln p_i)_{equilibrium}$$

We recognize that the stoichiometric coefficients of the reactants are negative and stoichiometric coefficients of the products are positive, and we can write these explicitly as follows:

$$\Delta G^0 = -\,R\,T\sum [\nu_i \ln p_i]_{equilibrium,products} - [\nu_i \ln p_i]_{equilibrium,reactants}$$

Taking advantage of the ln functions with opposite signs, we can write the summation as a ratio, and since x ln x is ln x^x, each pressure term is raised to the power of its stoichiometric coefficient.

$$\Delta G^0 = -\,R\,T\{\ln\frac{[p_i]^{\nu_i}{}_{equilibrium,\ products}}{[p_i]^{\nu_i}{}_{equilibrium,\ reactants}}\}$$

The ratio of pressure terms raised to the powers of the stoichiometric coefficients at equilibrium is exactly the thermodynamic equilibrium constant (K_p), and we write the final expression as follows:

$$\Delta G^0 = -\,R\,T\,ln\,K_p$$

The equilibrium constant is related to the change in the Gibbs free energies of the pure reactants and pure products, and hence, we can estimate this value without experimenting but from knowing the Gibbs free energies of chemical substances. Note that the equilibrium constant has no units! The plot of ΔG˚ vs ln K_p is linear with a slope of – RT (Figure 18.5).

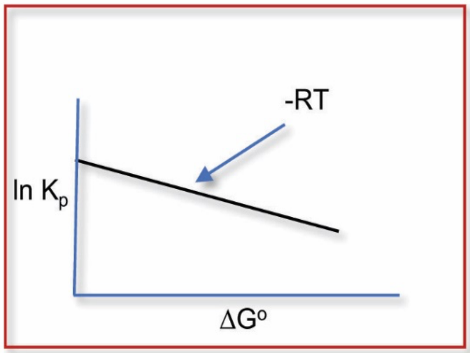


Figure 18.5 Plot of ΔG˚ vs ln K_p for a chemical reaction involving ideal gases. The negative slope indicating inverse relation, lesser the value of -ΔG˚, larger the equilibrium constant. The slope is given by -RT and directly depends on the temperature of the system.

Example 18.6

Calculate the change in the equilibrium constant when the reaction Gibbs free energy (ΔG˚) increases from RT to 3RT.

when ΔG˚ is RT, $K_p = e_p^{-\Delta G^\circ/RT} = e_p^{-RT/RT} = 0.37$

when ΔG˚ is 3RT, $K_{p'} = e_{p'}^{-\Delta G^\circ/RT} = e_{p'}^{-3RT/RT} = 0.05$

thus, subtracting the latter from the former, the change is $\Delta K_p = K_{p'} - K_p = 0.05 – 0.37 = -0.32$

The equilibrium constant decreases because the Gibbs free energy of the reaction is increased.

From a different viewpoint, taking anti-logs on both sides of the above relation, we can write K_p as an exponential function of Gibbs free energy of the reaction.

$$K_p = e^{(-\Delta G^0/R\,T)}$$

The exponential function indicates that small decreases in ΔG˚ cause large increases in K_p or that it increases exponentially with -ΔG˚. The lower the –ΔG˚ (more negative), the greater the equilibrium constant, and the equilibrium constant also depends on the temperature, explicitly.

For a simple reaction, A + B going to products C + D with their corresponding stoichiometric coefficients, the equilibrium constant, for example, is written in terms of their corresponding equilibrium partial pressures raised to their corresponding stoichiometric coefficients as follows:

$$K_p = ({p_D}^{\nu_D}\,{p_C}^{\nu_C})/({p_A}^{\nu_A}\,{p_B}^{\nu_B})$$

Example 18.7

Calculate the change in the equilibrium constant when the ΔG˚ decreased from - RT to -3RT. See the above example, and similarly, we get:

$K_p = e_p^{-\Delta G^\circ/RT} = e_p^{RT/RT} = 2.72$ and $K_{p'} = e_p^{-\Delta G^\circ/RT} = e_p^{3RT/RT} = 20.09$

ΔK_p = 20.09 – 2.72 = 17.37, more than an order of magnitude for a decrease of ΔG˚ by 2RT or ~ 5 kcal/mol.

The equilibrium constant increases when the Gibbs free energy of the reaction decreases.

18.5.3 Equilibrium constant for real gases and ΔG˚

The partial pressures of the ideal gas are replaced with fugacities to accommodate the non-ideal behavior of real gases. The equilibrium constant for real gases (K_f) in terms of the fugacity (f) at equilibrium is given below.

$$K_f = ({f_D}^{\nu_D}\,{f_C}^{\nu_C})/({f_A}^{\nu_A}\,{f_B}^{\nu_B})$$

Then, the ΔG˚ for real gases is written in terms of the ratio of equilibrium fugacities and the dependence of the equilibrium constant as well.

$$\Delta G^0 = -R\,T\ln K_f$$

$$K_f = e^{(-\,\Delta G^0/R\,T)}$$

Again, if we know the free energies of the pure substances, we can calculate the equilibrium constant without experimenting and this is the power of thermodynamics.

In summary, the overall Gibbs free energy change accompanying a chemical reaction is factored out into the mixing free energy and the reaction free energy. We found the relationship between the equilibrium constant and the decrease in the free energy of the system in terms of pure products and pure reactants. The composition of the equilibrium is precisely defined by the equilibrium pressures or equilibrium fugacities.

18.6 Equilibrium and Temperature

We will examine the equilibrium constant as a function of temperature so that by knowing its value at one temperature, we may be able to calculate its value at any other temperature. In the process, we will relate the equilibrium constant to enthalpy and entropy changes of the pure reactants and pure products. Thus, one can obtain the equilibrium constant at a temperature and estimate the reaction enthalpies and entropies as well. The study of the temperature dependence of the equilibrium (chemical or physical) is of immense importance in thermodynamics as well as for practical applications.

18.6.1 Temperature dependence of K_p

We start with the central relation connecting the equilibrium constant and the Gibbs free energy difference between pure products and pure reactants.

$$\Delta G^0 = -R\,T \ln K_p$$

We re-write the above with temperature and the equilibrium constant on opposite sides of the equation in preparation to differentiate the above expression with respect to temperature.

$$\ln K_p = -\frac{\Delta G^0}{R\,T}$$

Since ΔG° depends on temperature, we will write it in terms of temperature, explicitly, before differentiation using the fundamental equation involving ΔH° and ΔS°.

$$\ln K_p = -\frac{\Delta H^0 - T\Delta S^0}{R\,T}$$

The enthalpy and entropy changes are those of the pure substances, at equilibrium composition. Differentiating the above on both sides with respect to temperature, we get the following:

$$\frac{d}{dT}\left(\ln K_p\right) = -\frac{d}{dT}\left(\frac{\Delta H^0 - T\,\Delta S^0}{R\,T}\right)$$

We open the fraction in the parenthesis to cancel the temperature term in the numerator as follows:

$$\frac{d}{dT}\left(\ln K_p\right) = -\frac{d}{dT}\left(\frac{\Delta H^0}{R\,T} - \frac{T\Delta S^0}{R\,T}\right)$$

$$\frac{d}{dT}\left(\ln K_p\right) = -\frac{d}{dT}\frac{1}{R}\left(\frac{\Delta H^0}{T} - \Delta S^0\right)$$

When we consider a small temperature interval and given the shallow T-dependence of ΔH° and ΔS°, we can simplify the operand even further as follows:

$$\frac{d}{dT}\left(\ln K_p\right) = -\frac{\Delta H^0}{R}\frac{d}{dT}\left(\frac{1}{T}\right)$$

Integration of the above with limits T and T_o corresponding to the equilibrium constant, K_p and $K_p^{T_o}$, we get the following:

$$\ln K_p = \ln K_p^{T_0} - \frac{\Delta H^0}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)$$

Thus, ln K_p at any temperature T is related to standard temperature T_o and ΔH°, not a new relationship but seen before in a slightly different form. When $T > T_o$, then the parenthesis is negative and ln K_p increases or decreases depending on the sign of ΔH°. A plot of ln K_p vs 1/T (Figure 18.6) indicates a line with a slope equal to - $\Delta H^\circ/R$.

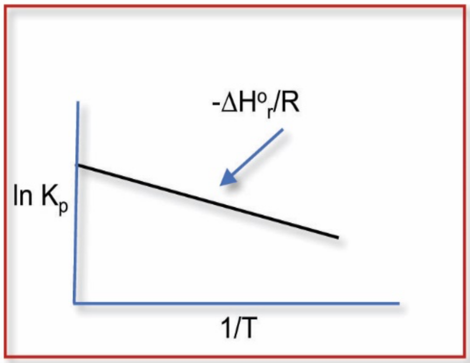


Figure 18.6 Plot of ln K_p vs 1/T for equilibrium involving ideal gases. The negative slope indicating an inverse relation with 1/T. When the reaction is endothermic (ΔH˚ >0), the slope is negative, and the equilibrium constant increases with an increase in T. The slope will be positive when ΔH˚<0 or exothermic, and the equilibrium constant decreases with an increase in temperature. The Y-intercept is ΔS˚/R.

We summarize our discussion of the temperature dependence of K_p as follows:

$$\ln K_p \ \uparrow when\ T \uparrow and\ \Delta H^{\circ} > 0, or\ endothermic$$

$$\ln K_p \ \downarrow when\ T \uparrow and\ \Delta H^{\circ} < 0, or\ exothermic$$

Example 18.8

Calculate how many-fold the equilibrium constant changes when the temperature is raised from 300 K to 330 K for reaction with a reaction enthalpy of 10 kJ/mol.

$$\ln K_{p_2}/K_{p_1} = -\frac{\Delta H^0}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) = -\frac{(-10)kJ}{mol}\left(\frac{1}{330\ K} - \frac{1}{300\ K}\right) = 1.44$$

The equilibrium constant increases by 1.44-fold because the net reaction is endothermic.

18.6.2 The van ‘t Hoff equation and ΔH˚

The last equation from the previous section is examined from a different vantage point to experimentally determine the equilibrium enthalpies. We re-write the above equation in the original differential form, assume that both ΔH˚ and ΔS˚ are independent of temperature, and obtain the following equation:

$$\frac{d}{dT}(\ln K_p) = \frac{\Delta H^0}{RT^2}$$

This is the van ‘t Hoff equation which relates the equilibrium constant with the enthalpy changes of the pure products and pure reactants, at equilibrium. One powerful application of the above equation is to obtain the enthalpy change by simply measuring the equilibrium constant at few temperatures by a non-calorimetric method. We discussed this approach under the heat of vaporization studies, earlier. The enthalpy obtained this way is the van 't Hoff enthalpy of the reaction (Figure 18.6).

The van ‘t Hoff equation is exactly valid when both ΔH˚ and ΔS˚ are independent of temperature and equilibrium is established. Over short ranges of temperature, these assumptions are reasonably valid and provides an approximate value for ΔH˚, the standard enthalpy of the reaction when measured at 1 atm and when pure substances are considered, under equilibrium. This a very important relation in examining the enthalpies of many biological and chemical equilibria, and a non-calorimetric method is sufficient to make these measurements. The latter is important because most calorimeters are expensive and only available to fewer laboratories around the world.

Example 18.9

Design an experiment to measure standard reaction enthalpy without a calorimeter.

Using the Van ‘t Hoff equation above, we can obtain ΔH˚ by measuring equilibrium constants at two or more temperatures. We shall integrate the equation with limits of K_p and $K_{p'}$ on the left and T_1 and T_2 on the right to get the integrated equation, as follows.

$$\ln K_{p'} = \ln K_p - \frac{\Delta H^0}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

A plot of ln K_p vs (1/T) gives a slope equal to - ΔH˚/R, a non-calorimetric method to measure enthalpy of a reaction.

18.6.3 Temperature dependence and the measurement of ΔS˚

From the equilibrium constant K_p and by measuring ΔH˚, we can obtain ΔS˚ by a non-calorimetric method by simple manipulation of thermodynamic quantities.

$$\Delta G^0 = (\Delta H^\circ - T\,\Delta S^\circ) = -R\,T\ln K_p$$

By rearranging, the terms we get the relation with enthalpy and entropy changes as before.

$$\ln K_p = -\left(\frac{\Delta H^\circ - T\Delta S^\circ}{RT}\right)$$

Expanding the fraction, we obtain a clearer expression for the entropy change.

$$\ln K_p = -\left(\frac{\Delta H^\circ}{RT}\right) + \left(\frac{\Delta S^\circ}{R}\right)$$

A plot of ln K_p vs 1/T will have a slope of - ΔH˚/R and an intercept of ΔS˚/R (Figure 18.6). These plots are referred to as the van ‘t Hoff plots and entropy changes are also measured from these plots. While the slope of the plot is more reliable, intercepts have larger errors, as a caution to the practitioner.

Example 18.10

Design an experiment to measure standard reaction entropy without a calorimeter.

Using the following equation, measure the equilibrium constant as a function of temperature over a short range, at constant pressure.

$$\ln K_p = -\left(\frac{\Delta H^\circ}{RT}\right) + \left(\frac{\Delta S^\circ}{R}\right)$$

A plot of ln K_p vs (1/T) gives intercept equal to ΔS˚/R, a non-calorimetric method to measure standard entropy of a reaction using equilibrium conditions. However, the intercept is sensitive to errors and high precision measurements and validity of the assumptions are required for reliable values.

In summary, inquiry into the Gibbs free energy changes of a chemical reaction led us to connect it with the equilibrium constant, which in turn led us to predict the equilibrium constant from the Gibbs free energy changes. Temperature dependence of the equilibrium constant led us to the reaction enthalpies and reaction entropies which are valid for equilibrium conditions. Thus, the entire thermodynamic picture of equilibrium is obtained by systematic thermodynamic analysis.

18.7 Effect of temperature on equilibrium vapor pressure

Using liquid-vapor equilibrium, we looked at the heat of vaporization in a previous chapter by using the barometric law. But now we work out a direct derivation of this important equation. Let the liquid be in equilibrium with its vapor, and as we change the temperature, the vapor pressure above the liquid will also change. As we heat the sample, some liquid molecules gain a certain amount of excess energy and escape into the gas phase. Thus, the vapor pressure increases as we increase the temperature, and when we cool the sample, some net number of gas molecules will condense into the liquid phase and the vapor pressure drops. Thus, the system is at equilibrium between the liquid phase and the gas phase at any given temperature, and this equilibrium can be shifted by adjusting the temperature up or down.

$$Liquid \rightleftharpoons Vapor$$

Since the vapor pressure changes with temperature but the concentration of the liquid does not change, we can write the equilibrium constant of the liquid-vapor equilibrium in terms of the vapor pressure.

$$K_p = p$$

At equilibrium, the chemical potential of the gas molecules is equal to the chemical potential of the liquid molecules, exactly, and it is a reversible process. We will ignore the change in the volume of the liquid with temperature because the change in the pressure of the vapor will be much greater than the change in the liquid volume as we change the temperature and write the following equation to account for the temperature effect on the equilibrium constant, from the previous section.

$$\ln(K_p / K_p^{T_0}) = -\frac{\Delta H^0}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)$$

However, for the liquid-vapor equilibrium, K_p can be replaced by p itself, and we recognize that the ln of the ratio of vapor pressures (p and p_{To}) at any two temperatures (T and T_o) is related by the heat of vaporization ΔH°_{vapor}, as follows:

$$\ln(p/p_{T_0}) = -\frac{\Delta H^0_{vapor}}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)$$

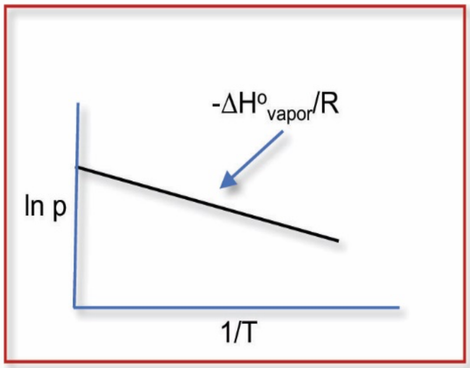


Figure 18.7 Plot of ln K_p vs 1/T for liquid-vapor equilibrium. The negative slope indicating an inverse relation with 1/T. When the reaction is endothermic ($\Delta H^{\circ} > 0$), the slope is negative and the equilibrium constant increases with an increase in T.

As a plot of the logarithm of vapor pressure versus 1/T, we get a straight line with slope and intercept as defined by the above equation (Figure 18.7). Since the heat of vaporization of most liquids is positive, the slope will be negative and the slope equals $-\Delta H^{\circ}_{vapor}/R$. The heat of vaporization can be measured by a non-calorimetric method by monitoring the vapor pressure as a function of temperature, as we discussed earlier.

Thus, vapor pressure decreases with an increase in the heat of vaporization but increases with an increase in temperature, and it is like what we deduced earlier. Taking anti-logs on both sides, writing p_{To} as p_o, we get the heat of vaporization as follows:

$$p = p_0\, e^{-\frac{\Delta H^0_{vapor}}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)}$$

In summary, ΔH° can be measured by a non-calorimetric method, and an expensive calorimeter is not required. However, some limitations of the method are that we assume that the liquid volume does not change during the heating and that the vapor behaves ideally, but corrections can be introduced for these approximations when more precise values are necessary.

18.8 Controlling the Equilibrium Composition

Next, we use the above assets to control the position of the equilibrium of a chemical reaction. This is what a chemist often does for a living, and the chemist is asked to control the direction of a chemical reaction as well as the equilibrium position. Although the effect of temperature and the effect of pressure on equilibrium constant are examined earlier, there are still other aspects to be discussed, as demonstrated below. We investigate these possibilities by writing the exact differential of ΔG as a function of T, p, and reaction progress (ξ), as follows:

$$d(\Delta G) = \left(\frac{\partial \Delta G}{\partial T}\right)_{p,\xi} dT + \left(\frac{\partial \Delta G}{\partial p}\right)_{T,\xi} dp + \left(\frac{\partial \Delta G}{\partial \xi}\right)_{T,p} d\xi$$

The net change in ΔG is due to changes in its value due to each of the three variables, T, p, and ξ, and we previously showed the following expression connecting reaction progress and reaction free energy.

$$dG/d\xi = \sum \nu_i\, \mu_i = \Delta G$$

Under constant T, and p conditions, we can write the above equation as follows:

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,p} = \Delta G$$

We replace ΔG in the last term of the exact differential of ΔG by $(dG/d\xi)_{T,p}$ as follows:

$$d(\Delta G) = \left(\frac{\partial \Delta G}{\partial T}\right)_{p,\xi} dT + \left(\frac{\partial \Delta G}{\partial p}\right)_{T,\xi} dp + \frac{d}{d\xi}\left(\frac{\partial G}{\partial \xi}\right) d\xi$$

The third term on the right is simply the second derivative of G with respect to reaction progress and we indicate it as G" for simplicity.

$$d(\Delta G) = \left(\frac{\partial \Delta G}{\partial T}\right)_{p,\xi} dT + \left(\frac{\partial \Delta G}{\partial p}\right)_{T,\xi} dp + G''\, d\xi$$

This equation describes how the reaction free energy is controlled by the variables T, p, and the reaction progress, and we will examine these details for a chemical equilibrium in the subsequent sections.

18.8.1 Effect of pressure on the equilibrium composition

Since we are looking for the effect of pressure on the equilibrium, we are looking for the change in the equilibrium composition with respect to pressure. We start where we left off but impose constant composition conditions or when the progress of the reaction is arrested (dξ =0).

$$d(\Delta G) = \left(\frac{\partial \Delta G}{\partial T}\right)_{p,\xi} dT + \left(\frac{\partial \Delta G}{\partial p}\right)_{T,\xi} dp + 0$$

Comparing the above with the differential of ΔG with respect to T and p from a previous section, we recognize that the values of the first two terms in both equations must be the same under constant composition conditions.

$$d(\Delta G) = -\Delta S\, dT + \Delta V\, dp$$

Therefore, we can replace the first and the second terms in the penultimate equation with ΔS and ΔV terms from the above equation, and obtain the following simpler relation to achieve our goal as follows:

$$d(\Delta G) = -\Delta S\, dT + \Delta V\, dp + G''\, d\xi$$

At constant T (dT =0) and at equilibrium (dΔG = 0), we obtain the simplified relation as follows:

$$\mathrm{d}(\Delta G) = 0 = \Delta V\, dp + G''\, d\xi$$

By rearranging, we see that the change in the progress with pressure at constant T is given in terms of the volume change, ΔV, getting nearer to our goal.

$$G''\, d\xi = -\Delta V\, dp$$

$$\left(\frac{d\xi}{dp}\right)_T = -\frac{\Delta V}{G''}$$

The second derivative of G with respect to reaction progress (G") is >0 because the plot of G vs reaction progress is concave upward (Figures 18.3, and 18.4).

$G'' > 0$ for upward concave functions

The plot of ξ versus p will be linear over a small range of pressures because V depends on p as well. But the slope of the plot will depend on ΔV with three different possibilities. The plot should be linear with a positive slope, when ΔV <0 (Figure 18.8) or it will have a negative slope when ΔV >0 (Figure 18.9). When volume increases during a reaction, an increase of pressure will move the equilibrium in the reverse direction to offset the increase of pressure because the decrease in volume reduces the pressure applied on the system or this is the stimulus response by the system.

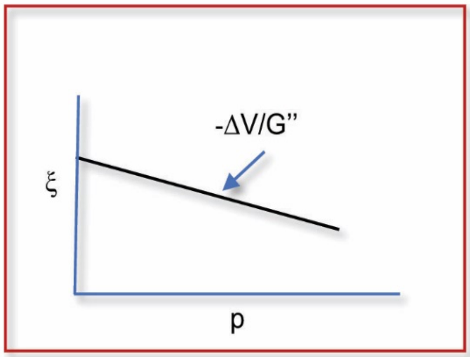


Figure 18.8 Plot of reaction progress vs pressure for an equilibrium, involving ideal gases. Because G" is >0, the slope of the plot will be negative when ΔV >0 (left). The equilibrium will move in reverse when pressure increases. Thus, the system will move to compensate for the external influences.

Conversely, when the volume decreases (ΔV <0) during a reaction, the increase of pressure moves the equilibrium in the forward direction and the slope will be positive. Thus, the system tends to compensate for the decrease in pressure, and thus it moves to compensate for the external effects applied on it.

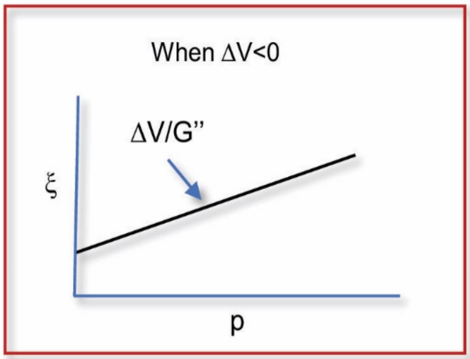


Figure 18.9 Plot of reaction progress vs pressure for an equilibrium, involving ideal gases. Because G" is >0, the slope of the plot will be positive when ΔV <0, and the equilibrium will move forward (right). Thus, the system will move to compensate for the external influences.

These deductions are summarized by the following conditions for easy recognition:

$$\xi \downarrow when\ p \uparrow and\ \Delta V > 0$$

$$\xi \uparrow when\ p \uparrow and\ \Delta V < 0$$

However, we can readily see that when ΔV =0, the slope of either plot will be zero, and there will be no effect of pressure on the composition of the equilibrium. The effect of pressure on an equilibrium that is volume-neutral or ΔV =0 or isochoric is obvious. Thus, the effect of pressure on the equilibrium position is quantified but depends on the volume change as the reaction occurs. We can move the equilibrium to the right or the left or leave it alone by adjusting the pressure on the system, but this adjustment depends on the change in the volume of the reaction.

18.11 Calculate the rate of change of the reaction progress per atm when a reaction has ΔV = 2 L and G" = 1 kcal.

We are asked to get the rate of change of progress with respect to pressure. We use the following equation and substitute the values of G" = 1 kcal, ΔV = 2 L.

$$\left(\frac{d\xi}{dp}\right)_T = -\frac{\Delta V}{G''}$$

The answer is -2 L/kcal. The answer is correct because the units match with the first derivative of progress with respect to pressure, where pressure is expressed in terms of energy per unit volume (1/p = V/nRT). Because volume increases in the reaction, increase of pressure decreases the progress.

18.8.2 Effect of temperature on the equilibrium position

The effect of T on the equilibrium composition is analyzed similarly, as the effect of pressure we examined in the previous section. Again, this is important in controlling the position of the equilibrium of a given chemical reaction or a physical process. We write the exact differential of ΔG as a function of T, p, and reaction progress.

$$d(\Delta G) = -\Delta S\, dT + \Delta V\, dp + G''\, d\xi$$

Imposing the equilibrium conditions, we set ΔG =0, and imposing the constant pressure conditions (dp =0), we get the following:

$$\Delta G = 0 = -\Delta S\, dT + G''\, d\xi$$

The negative sign is absorbed by shifting the ΔS term to the other side of equality.

$$G'' d\xi = \Delta S\, dT$$

Rearranging the terms, we get the partial derivative of reaction progress with respect to T at constant pressure, and we replace ΔS with ΔH/T, again using ΔG =0.

$$\left(\frac{d\xi}{dT}\right)_p = \frac{\Delta S}{G''} = \frac{\Delta H}{T\, G''}$$

As in the case of pressure dependence, the slope of the plot of progress vs temperature will be linear over a narrow temperature range and the slope of the plot is ΔH/G". Three scenarios are possible. The slope will be positive when ΔH >0 (Figure 18.10). The equilibrium will move forward with an increase in temperature and more products will be formed and the enthalpy supplied will be used to make more products because the forward reaction is endothermic or ΔH >0.

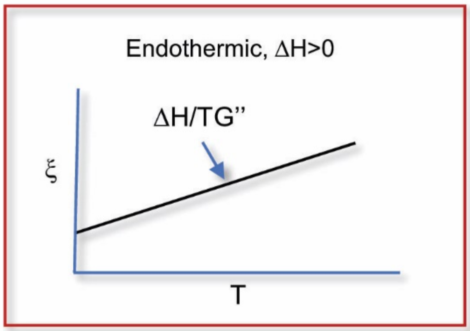


Figure 18.10 Plot of reaction progress vs temperature for an equilibrium process, involving ideal gases. Because G" is >0, the slope of the linear plot will be positive when ΔH >0. The equilibrium will move forward with an increase in temperature and make more quantities of products. Thus, the equilibrium will move to compensate for the external influence.

Example 18.12

Calculate the change in the reaction progress per K when a reaction has ΔS = 2 kcal/K and G" =1 kcal.

Values are: G" =1 kcal, ΔS = 2 kcal/K, value asked is the rate of change of progress with respect to temperature in kelvin. We use the following equation and substitute the values.

$$\left(\frac{d\xi}{dT}\right)_p = \frac{\Delta S}{G''}$$

The final answer is 2/K. The units match with the above first derivative because progress is dimensionless.

When heat is released during the reaction (exothermic, ∆H<0), the slope of the plot of progress vs temperature will be negative (Figure 18.11). Thus, an increase in temperature will diminish the progress of the forward process and move the equilibrium in the reverse direction to compensate for the enthalpy supplied. This is because the reverse reaction absorbs the supplied enthalpy (endothermic) and makes more quantities of the reactants. Again, the equilibrium moves to compensate for the external stimulus applied.

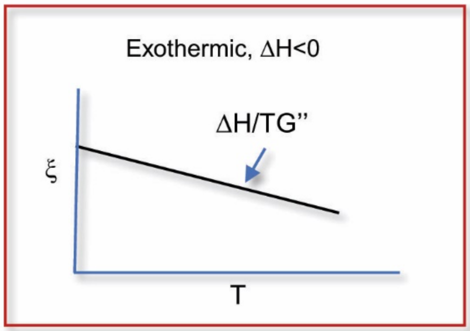


Figure 18.11 Plot of reaction progress vs temperature for an equilibrium process, involving ideal gases. Because G” is >0, the slope of the plot will be negative when ∆H <0 (left). The equilibrium will move in the reverse for exothermic reactions when the temperature increases. Thus, the equilibrium will move to compensate for the external influences.

Conversely, when heat is absorbed (endothermic, ∆H>0), an increase of temperature moves the equilibrium in the forward direction. Thus, the system tends to compensate for the external effects applied to the system. These can be summarized by the following.

$$\xi \uparrow \textit{when } T \uparrow \textit{when } \Delta H > 0 \textit{ or endothermic}$$

$$\xi \downarrow \textit{when } T \uparrow \textit{when } \Delta H < 0 \textit{ or exothermic}$$

There will be no effect of temperature on equilibrium which is thermo-neutral or ∆H =0 or isenthalpic. Thus, the effect of temperature on the equilibrium position is quantified but depends on the enthalpy change as the reaction occurs. We can move the equilibrium to the right or the left by changing the temperature, depending on if the reaction is exothermic, endothermic, or thermo-neutral.

In summary, we looked at the effect of pressure and temperature on the reaction progress for chemical equilibrium. The position of the equilibrium will move in such a manner as to compensate for the external influences but predictable without experimenting, again demonstrating the power of thermodynamics.

18.9 Calorimetric measurements of K_p and ΔS°

In this section, we will look at experimental measurements of equilibrium constants using calorimetry, which we encountered earlier. We write the fundamental equation and get the following equations from it. The superscript represents the standard conditions of 1 atm pressure for the measurement of these quantities.

$$\Delta G^0 = \Delta H^0 - T\,\Delta S^0$$

$$-R\,T\ln K_p = \Delta G^0 = \Delta H^0 - T\,\Delta S^0$$

Rearranging the terms, we get the equilibrium constant in terms of enthalpy and entropy changes.

$$\ln K_p = -(\Delta H^0/R\ T) + (\Delta S^0/R)$$

We measure enthalpy changes directly with a calorimeter and then estimate ΔS˚ by applying the third law as illustrated below. ΔSº is written in terms of the entropies of pure products and pure reactants at temperature T as follows:

$$\Delta S^0 = \Delta S^0_{products} - \Delta S^0_{reactants}$$

In modern calorimetry, there is a workaround for the above problem of applying the third law. First, ΔH is measured as a function of the concentration of one of the reactants while the other reactants are in excess. At low concentrations of the limiting reagent, ΔH is approximately equal to the reaction enthalpy because all of the limiting reagent is consumed by the other reagents that are present in excess. A plot of ΔH as a function of the concentration of the limiting reagent gives an isotherm and the isotherm is fitted with specific equilibrium models. Best fits of the model to the data are used to obtain the equilibrium constant and then the corresponding ΔG˚. From these values of ΔG˚ and Kp, one obtains ΔS˚ using the fundamental equation (G=H-TS). Thus, ΔS˚ can be obtained experimentally, without applying the third law, but this requires careful mathematical modeling of the equilibrium, which is not discussed in this book.

18.10 Solid-Gas Equilibrium: Limestone Decomposition

An example of the industrial significance of shifting the equilibrium by controlling the reaction conditions is the decomposition of solid calcium carbonate (solid) to give calcium oxide (solid) and carbon dioxide (gas). Calcium oxide is a bulk industrial chemical used to make a variety of products while limestone is abundant on this planet and mined in very large quantities. Since the partial pressure of carbon dioxide increases as the reaction progresses, or pressure increases with progress, and all other components are solids, the equilibrium constant is dictated solely by the pressure of carbon dioxide. The concentrations of other substances do not change during the reaction because they are in solid form.

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

The value of Kp =p, where p is the partial pressure of carbon dioxide. We use the previous discussion to calculate ln Kp and get ΔG˚ as well as all the other thermodynamic quantities from it.

Example 18.13

Calculate the equilibrium constants for the decomposition of limestone to calcium oxide and carbon dioxide when the partial pressure of CO_2 is 0.01 atm at 300 K and 1.1 atm at 500 K.

The balanced chemical equation for the above reaction is as follows:

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

Since limestone and CaO are in the solid phase, their concentrations do not change as we heat the reaction mixture. Thus, $K_p = p(CO_2)$ atm/1 atm, and K_p at 300 K is 0.01 and K_p at 500 K is 1.1.

Example 18.14

Calculate ΔG˚ for the above example at 500 K, when pure products are formed from pure reactants.

$$\Delta G^\circ = -R\,T\ln(Kp) = -8.3144\frac{J}{K\ mol} * 500\ K * \ln\left(\frac{1.1\ atm}{1\ atm}\right) = -396\ J/mol$$

18.11 Molecular interpretation

Chemical reactions occur because of a decrease in Gibbs free energy during the progress of the reaction, but this decrease could be due to the chemical reaction as well as the mixing that occurs as the reaction progresses. Thus, the progress of the chemical reaction, at least at the early stages of the reaction, could be just due to mixing free energy alone when the chemical reaction is endergonic. However, equilibrium is established when there is no further change in the Gibbs free energy, and the equilibrium constant is related exponentially to the decrease in the reaction free energy. At the molecular level, these discussions point out that as the electronic distribution and the nuclear coordinates of the reactants change to produce products during the chemical reaction, the changes are favored if the net value of the Gibbs free energy is reduced. The reaction can also proceed to some extent by simple mixing of the reactants and products as discussed above. Thus, mixing could also facilitate the chemical reaction in addition to the changes in the coordinates of the electrons and nuclei in the reactants.

Thus, the popular argument that the chemical reactions occur because products are of lower Gibbs free energy than the reactants is not entirely correct because of the role of the mixing free energy in driving the chemical reaction. Therefore, by and large, a decrease in the potential and kinetic energies of the nuclei and electrons in molecules accounts for the reaction free energy and drives the reaction favored when the sum of these energies is decreased. Thus, at the molecular level, the energies of electrons and the nucleons in their mutual potentials dictate the free energy changes and provide the intrinsic drive for the chemical reaction to move forward or in reverse. These days, we can readily compute approximate values of the free energy changes with moderately powerful computers that are in reasonable agreement with experimental values.

The same arguments apply for the establishment of equilibrium because it has two reactions proceeding simultaneously, in opposite directions, at the same rate. At equilibrium, the reaction mixture has electrons and nuclei with the lowest possible kinetic and potential energies under the conditions of pressure, temperature, and composition as well as their random distribution in the mixture (mixing free energy). Any further decrease in free energy is not possible unless the equilibrium conditions are changed, such as raising or lowering temperature, pressure, or changing the concentrations of the reactants or products. These changes, in turn, trigger further changes in Gibbs free energy until there are no more changes and the equilibrium is re-established under the new set of reaction conditions.

The effect of equilibrium pressure can be examined at the molecular level. For a reaction that undergoes expansion of volume as it proceeds, the application of pressure will reverse it. This is because the products occupy more volume than the reactants, usually due to the increase in the mole numbers as the reaction moves forward. As an increase in pressure increases the Gibbs free energy, the system moves to lower free energy by converting some of the products to reactants and storing the excess energy as potential and kinetic energies of the electrons and nucleons. The reverse is true for reactions with $\Delta V < 0$. In all situations, the kinetic and potential energies of the fundamental particles of atoms and molecules change to accommodate the external stimulus that is applied to the system.

An increase of temperature, for example, raises the kinetic energy of the molecules (ideal gas) and in case of an endothermic reaction, this excess heat is utilized to make reactants, shifting the equilibrium to the products' side. The equilibrium moves in the forward direction to store that extra energy in the potential and kinetic energies of the electrons and nucleons of the products, and a new equilibrium position is established. The argument is reversed for exothermic reactions. Thus, when we change the temperature, pressure, or composition, we are trading the energies of the fundamental particles, and molecular level descriptions aid in the understanding of the effect of temperature on the equilibrium which provides a conceptual visualization. Thus, thermodynamics and quantum mechanics are intrinsically connected at the hip.

18.12 Applications in daily Life

Equilibria are everywhere in our daily lives, and they are constantly being shifted by either pressure, temperature, or other stimuli. The cloud formation in the upper atmosphere, for example, is due to a change in the mole numbers of water molecules coupled with changes in the temperature. The equilibrium between water vapor and water droplets is influenced by these changes. When these droplets grow to large enough size that the earth's gravity can pull them down, we experience rain.

All distillations are at equilibria, and this is a major industrial method to fractionate petroleum and numerous other substances, such as alcohol. Crystallization is another equilibrium process that is shifted toward the solid phase in many industrial processes to obtain purer substances. The human body is maintained at 37 ˚C and this requires a constant supply of enthalpy to keep it away from equilibrium with room temperature. Most biochemical processes occur away from the equilibrium but that requires a constant decrease in the Gibbs free energy. Thus, shifting the equilibrium is a constant struggle of life.

Oceans are at thermal equilibrium with the atmosphere above them and the liquid water is in equilibrium with the humidity of the air above it. When there is a change in the temperature of the water or the pressure of the atmosphere, storms can develop and utilize the excess Gibbs free energy that is made available due to the temperature and/or pressure changes. Some of this free energy is utilized, in turn, by the gusting winds to topple trees or lift boats out of docks and onto the streets. Thus, Gibbs free energy change is responsible for the changes we notice around us.

18.13 Key points

1. The concepts of chemical potential and reaction progress are important in chemistry, physics, and biology. The progress of the reaction defines the rate of a chemical reaction and the rate of change of chemical potential defines the direction of the reaction.
2. The progress of a chemical reaction is zero when the reaction is about to begin, and it is unity when the reaction is complete. Thus, the reaction progress defines the degree of completion of the reaction.
3. The endoergonic reactions are not favorable but the mixing free energy can move the reaction forward and establish the equilibrium.
4. By removing one of the products from the reaction mixture, the equilibrium can be re-established forming more of that product. Thus, even endoergonic reactions can be driven toward completion by continuous depletion of product from its equilibrium mixture.
5. The standard free energy of the reaction is related to the equilibrium constant, exponentially. Hence, small decreases in the reaction free energy can shift the equilibrium constant by a large amount.
6. The equilibrium shifts in such a manner to offset the stimulus applied on the system. For example, for reactions where the volume increases, a decrease of pressure moves the equilibrium to the products. The addition of products to the reaction mixture shifts the equilibrium toward the reactants. This is the famous Le Chatelier's principle.

18.14 Key terms and units

The equilibrium constant, chemical potential, enthalpies, and entropies of reactions. The thermodynamic equilibrium constant K_p is dimensionless, contrary to the popular misconception. Logarithmic function in $\Delta G^\circ = -RT \ln K_p$ can't be applied if K_p has units and the equilibrium constant is to be written in terms of standard concentrations, moles per cubic meter, or reactants and products. For example, the reactant and product concentrations are to be divided by their respective standard concentrations so that the ratio of their concentrations is dimensionless, regardless of the number of products or reactants present in the equilibrium. For gaseous products and reactants, their partial pressures are divided with the standard pressure of 1 atm so that the equilibrium constant is dimensionless. This is the thermodynamic equilibrium constant, different from the equilibrium constants that are often discussed in the biological sciences.

$$\nu_A\, A + \nu_B\, B \rightarrow \nu_c\, C + \nu_D\, D$$

$$dG = \sum \mu_i\, dn_i$$

$$\frac{dG}{d\xi} = \sum \nu_i\, \mu_i$$

$$\Delta G_{reaction} = \Delta G^0 + R\,T \sum \nu_i \ln p_i$$

$$K_p = (p_D{}^{\nu_D}\, p_C{}^{\nu_C})/(p_A{}^{\nu_A}\, p_B{}^{\nu_B})$$

$$\Delta G^0 = -R\,T \ln K_p$$

$$\ln K_p = \ln K_p^{T_0} - \frac{\Delta H^0}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)$$

$$\ln K_p = -\left(\frac{\Delta H^\circ}{RT}\right) + \left(\frac{\Delta S^\circ}{R}\right)$$

$$\left(\frac{d\xi}{dp}\right)_T = -\frac{\Delta V}{G''}$$

$$\left(\frac{d\xi}{dT}\right)_p = \frac{\Delta S}{G''} = \frac{\Delta H}{T\,G''}$$

$$\ln K_p = -(\Delta H^0/R\ T) + (\Delta S^0_{0\ to\ T}/R)$$

18.15 Self Reflection

1. Explain to a Gen Chem student why chemical reactions occur, even when the reaction is endothermic, use chemical potential as the key parameter.
2. What are the merits of using Gibbs free energy over entropy to predict the spontaneity of a chemical reaction?
3. Discuss why enthalpy or internal energy can't be used successfully to explain the natural direction of a chemical reaction.
4. Given the space of your car, discuss the processes taking place with a decrease in chemical potential when the car is running as opposed to parked.
5. Given that the universe is fast expanding, discuss how the chemical potential of the universe is changing.
6. Given the Gen Chem lab, what experiments can you design to demonstrate the decrease in the chemical potential as a chemical reaction proceeds and achieves equilibrium? Explain how you plan to shift the equilibrium forward or reverse by changing one of the thermodynamic parameters of the system.
7. Plot H vs ξ, H vs G, S vs ξ and μ vs ξ and explain the plots for an endothermic reaction as well as for an exothermic reaction.
8. Design a Gen Chem experiment to demonstrate the enthalpy of mixing for an endothermic process and an exothermic reaction.
9. How do you explain that mixing salt and water lowers the free energy of the system to a class of high school seniors?

18.16 Further Reading

1. https://ocw.mit.edu/courses/chemistry/5-60-thermodynamics-kinetics-spring-2008/lecture-notes/5_60_lecture16.pdf
2. https://ocw.mit.edu/courses/chemistry/5-60-thermodynamics-kinetics-spring-2008/video-lectures/lecture-15-chemical-equilibrium/
3. https://ocw.mit.edu/courses/chemistry/5-60-thermodynamics-kinetics-spring-2008/video-lectures/lecture-16-temperature-pressure-and-kp/
4. https://en.wikipedia.org/wiki/Le_Chatelier%27s_principle

18.17 Self Tests

1. Chemical reactions are usually driven by these two kinds of Gibbs free energy changes, under constant p and T conditions,

a. solvation free energy

b. evaporation free energy

c. reaction free energy

d. mixing free energy

e. none of these

2. The equilibrium constant can be precisely calculated from the

a. reaction Gibbs free energy

b. reaction enthalpy because products are more stable

c. reaction energy because reactants are less stable

d. reaction entropy because the products are more random than the reactants

e. none of these

3. The effect of temperature or pressure on the equilibrium is readily obtained, because this thermodynamic quantity is related to the equilibrium constant

a. ΔG
b. ΔG°
c. ΔH°
d. ΔS°
e. none of these

4. The mixing Gibbs free energy of all gases is
   a. zero
   b. positive
   c. negative
   d. infinity
   e. none of these

5. When a chemical reaction occurs, the net Gibbs free energy change is due to
   a. the chemical reaction only
   b. the mixing of the reactants
   c. the products that are more stable
   d. the reaction as well as the mixing of reactants and products
   e. none of these

6. The mathematical representation of a chemical reaction consisting of i chemicals (A_i) with their corresponding stoichiometric coefficients (v_i) is
   a. $\sum v_i A_i$
   b. $\sum v_i A_i = 0$
   c. $\sum v A_i = 0$
   d. $\sum A_i$
   e. none of these

7. Chemical reaction is spontaneous in the forward direction when
   a. $\Delta G_{reaction} = 0$
   b. $\Delta G_{reaction} > 0$
   c. $\Delta G_{reaction} < 0$
   d. can't say
   e. none of these

8. The rate of change of reaction free energy with reaction progress is given by
   a. $\frac{dH}{d\xi} = \sum \nu_i \mu_i$
   b. $\frac{dG}{d\xi} = \sum \nu_c \mu_i$
   c. $\frac{dG}{d\xi} = \sum \nu_n \mu_i$
   d. $\frac{dG}{d\xi} = \sum \nu_i \mu_i$
   e. none of these

9. The plot of G vs reaction progress for an exoergonic reaction has slope
   a. >0
   b. =0
   c. <0
   d. infinity
   e. none of these
10. The plot of G vs reaction progress for an endoergonic reaction has slope
   a. >0
   b. =0
   c. <0
   d. infinity
   e. none of these
11. The following is the equation describing the Gibbs free energy for equilibrium (ΔG°) and its equilibrium constant (Kp) at temperature T:
   a. $\Delta G^0 = R\,T\,ln\,K_p$
   b. $\Delta G^0 = -R\,T\,ln\,K_p$
   c. $\Delta G^0 = -R\,T/\,ln\,K_p$
   d. $\Delta G^0 = R\,T\,ln\,K_p$
   e. none of these
12. Plot of ΔG° vs ln Kp, where the latter is the equilibrium constant is linear with a slope equal to
   a. RT
   b. R/T
   c. ln K_p
   d. zero
   e. none of these
13. The equilibrium constant increases
   a. exponentially with temperature
   b. linearly with ΔG°
   c. unpredictably with Gibbs free energy of the reaction
   d. exponentially with increase in ΔG°
   e. none of these
14. The thermodynamic equilibrium constant has
   a. no value
   b. value of one
   c. dimension less
   d. dimensions of inverse mole numbers
   e. none of these

15. When temperature increases, the equilibrium constant of an exothermic reaction
    - a. remains the same
    - b. increases linearly with inverse of temperature
    - c. increases exponentially
    - d. increases linearly with temperature
    - e. none of these
16. When log (equilibrium constant) is plotted against 1/temperature, the slope is related to
    - a. entropy
    - b. van ‘t Hoff entropy
    - c. van ‘t Hoff enthalpy
    - d. van ‘t Hoff free energy
    - e. none of these
17. When log(equilibrium constant) is plotted on the y-axis against 1/T on the x-axis, the y-intercept is related to the
    - a. reaction entropy
    - b. reaction enthalpy
    - c. van ‘t Hoff enthalpy
    - d. reaction free energy
    - e. none of these
18. When the vapor is in equilibrium with its liquid, the vapor pressure (p) related to the enthalpy of vaporization is connected to temperature (T) by the following equation,
    - a. $pV = \Delta H\ RT$
    - b. $\Delta H^\circ = - nRT$
    - c. $p = p_0\, e^{-\frac{\Delta H^0_{vapor}}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)}$
    - d. $p = p_0\, e^{-\frac{\Delta H^0_{vapor}}{R}\left(\frac{1}{T}+\frac{1}{T_0}\right)}$
    - e. none of these
19. Plot of reaction progress on y-axis vs pressure, at constant T, on the x-axis has a slope
    - a. proportional to – (change in the volume) when the reaction proceeds
    - b. proportional to change in the volume when the reaction proceeds
    - c. proportional to change in the mole numbers as the reaction proceeds
    - d. zero
    - e. none of these
20. The plot of reaction progress vs temperature for a reaction has a slope proportional to
    - a. temperature
    - b. pressure
    - c. reaction enthalpy

d. reaction volume

e. none of these

21. The change in the equilibrium constant when ∆G˚ increases from RT to 3RT is

a. 0.037

b. 0.05

c.-0.32

d. 0.37

e. none of these

22. The change in the equilibrium constant for the reaction $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ when the partial pressure of CO_2 increases from 0.01 atm to 1.1 by heating from 100 K to 500 K, respectively, is

a. 0.037

b. 0.005

c.-0.37

d. 0.37

e. none of these

23. The equilibrium constant for the reaction $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ when the partial pressure of CO_2 is 0.01 atm at 100 K is

a. 0.037

b. 0.005

c.-0.37

d. 0.01 atm

e. none of these

24. The change in the equilibrium constant when ∆G˚ decreases from -RT to -3RT is

a. 0.037

b. 17.37

c.-17.37

d. 0.37

e. none of these

25. For a reaction with ∆V = 2 L, the second derivative of G with respect to progress equals to 1 kcal andthe rate of change of the reaction progress with respect to pressure is

a. -2 L/kcal

b. -0.2 / L

c. 1 L/atm

d. -3 L

e. none of these

26. For a reaction with ∆S = 2 kcal/K, the second derivative of G with respect to progress equals to 1 kcal and the rate of change of the reaction progress with respect to temperature is

a. -2/K

b. -0.2 / L

c. 1 L/atm

d. -2/kcal

e. none of these

18.18 Self Tests Key

1. d, 2. a, 3. b, 4. c, 5. d, 6. b, 7. c, 8. d, 9. c, 10. a, 11. b, 12. e, 13. e, 14. c, 15. e, 16. c, 17. a, 18. c, 19. a, 20. c, 21. c, 22. e, 23. e, 24. b, 25. a, 26. e

18.19 Problems

1. The change in the equilibrium constant when ΔG˚ increases from RT to 3RT is (Ans. -0.32)
2. The change in the equilibrium constant for the reaction $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ when the partial pressure of CO_2 increases from 0.01 atm to 1.1 by heating from 300 K to 500 K, respectively, is (Ans. 1.09)
3. The equilibrium constant for the reaction $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ when the partial pressure of CO_2 is 1 atm at 450 K is (Ans. 1)
4. The change in the equilibrium constant when ΔG˚ decreases from -RT to -3RT is (Ans.17.37)
5. If for a reaction ΔV = 2 L and the second derivative of G with respect to reaction progress equals to 1 kcal, what is the rate of change of the reaction progress with respect to pressure at constant temperature? (Ans. -2 L/kcal)
6. A reaction was characterized with ΔS = 2 kcal/K and second derivative of G with respect to progress has been 1 kcal. What is the rate of change of the reaction progress with respect to temperature at constant pressure for this reaction? (Ans. none of these)
7. The enthalpy of decomposition of calcium carbonate is 178 kJ/mol at 830 ˚C. If the partial pressure of carbon dioxide in equilibrium with calcium carbonate and calcium oxide at this temperature is 34 kPa, what is ΔS˚ for this reaction at 830 ˚C? (Ans. 152 J/mol K)
8. The ratio of equilibrium constants at 300 K to 330 K was 2.000. What is the ΔH˚ for this reaction? (Ans. 19.02 kJ/mol)
9. The ΔG˚ for a reaction at 300 K is changed from -10 kJ/mol to -20 kJ/mol at constant temperature. How many-fold does the equilibrium constant increase or decrease? (Ans. increases by nearly 55-fold).
10. Calculate ΔG˚ and $\Delta G_{reaction}$ when two ideal gases of 1 mol each with a partial pressure of 1 atm each, react halfway as follows, at 300 K. (μA = 1 kJ/mol; μB = 4.5 kJ/mol; μC = 1 kJ/mol at 300 K, 5 atm) $1\,A + 2\,B \rightarrow 2\,C$. (Ans. ΔG˚ = -8 kJ/mol; ΔGreaction=-2.8 kJ/mol)

19. Phase Equilibria

After completing this chapter, you will be able to:

- Recognize the conversion of a pure phase into another phase.
- Assess the relation between the chemical potential, the driving potential of phase transitions (not driving force, because there is no force acting on them), and the phase transition temperatures.
- Recognize the plots of chemical potential versus phase transition temperature.
- Identify the effect of pressure on phase transition temperature.
- Recognize and evaluate the Clapeyron equation and connect the volume and the entropy changes of phase transitions with the corresponding changes in enthalpies.

Goals

- Illustrate how chemical potentials of pure phases depend on temperature, at constant pressure.
- Identify the melting point, boiling point and the sublimation point on the μ *vs* T diagram.
- Examine the effect of pressure on the phase transition temperatures.
- Synthesize the Clapeyron equation and integrate it to predict the effect of pressure and temperature on ΔH, ΔS and ΔV of phase transitions and phase transition temperature.
- Devise a non-calorimetric method to estimate ΔH and ΔS of the phase transitions.

19.1 Why study this?

Raining, snowing, and water evaporation are all phase transitions taking place around us. These transitions are spontaneous processes and hence we ask the question, what drives these transitions? Since we know that the Gibbs free energy change or the chemical potential change determines the direction of a natural process, we will rely on this fundamental property of the system to investigate how phase changes are induced or controlled. What property of the system controls the phase transformation from solid to liquid, liquid to gas, or gas to a solid, and what is the qualitative reasoning for this process? In other words, why do natural processes of evaporation, raining, and snowing occur, and what is the driving potential behind these phase transitions? How do we control these phase transformations on a thermodynamic scale? These are inquisitive questions that allow us to investigate the spontaneous processes occurring around us. The phase transitions are also of great significance in practical applications and daily life, as will be discussed here.

The chemist is often asked to purify a given substance from a mixture of substances, for example, and he or she takes advantage of the fact that phase transitions occur among pure phases and exploits these transitions for the purification of substances. The separation of various fractions of petroleum from crude oil takes advantage of the fact that the boiling points of hydrocarbons increase with their molecular weight, roughly. Thus, different distillation fractions are separated using phase transitions on an industrial scale to produce various petroleum products, which is a trillion-dollar industry around the world. The production of alcohol from the fermentation broth is another classic example of purification by a phase transition that got the bootleggers into trouble. Modern craft beer production exploits this thermodynamic analysis. The boiling of liquid air is used to separate nitrogen from the air on an industrial scale to produce industrial gases.

Similarly, crystallization, sublimation, or freeze drying is often used for the purification of solid substances such as pharmaceuticals and fine chemicals which is, again, a trillion-dollar industry. We ask how these processes are controlled rationally for practical applications or fundamental studies. Thus, this chapter will be relevant to understand the natural phase changes occurring around us, in the lab or industry, as well as in the design and control of key industrial processes of high importance.

19.2 Chemical Potentials and Phase Equilibria

The conversion of one pure phase to another, at constant temperature and pressure, is called a phase transition. One example is the conversion of a solid to a liquid at its melting point. In this chapter, we ask why a given phase is stable at a given temperature and pressure, and under what conditions it becomes unstable and will transition to another phase. Since all natural processes are under the control of chemical potential, we will examine the chemical potentials of different phases of a pure substance, and study how the chemical potential of a phase is affected by temperature and pressure. The motivation for this discussion is to understand the relationship between the chemical potential and stability of a given phase of a pure substance to answer the above questions.

We also recognize that when a phase transition occurs under specific temperature and pressure, the chemical potentials of the two phases are equal. The system is at equilibrium as long as the two phases are present under these conditions. The phase that has the lowest chemical potential will dominate the equilibrium mixture. Thus, we will be examining the phase equilibrium in the light of the chemical potentials of the phases that are present in the system. The transition completes when we move above or below the characteristic temperature called the phase transition temperature. With these expectations, we move forward and examine the relationship between the chemical potential of a phase, pressure, and temperature of the system.

19.3 Stabilities of Phases of Pure Substances

First, we will compare the chemical potentials of different phases of a pure substance as a function of temperature at constant pressure. Then, we can deduce at what temperature one phase is more stable than the other, and hence when to expect the phase transition to occur. When you heat a sample of ice kept at -10˚C and 1 atm, for example, you convert it to the liquid phase when it reaches 0 ˚C and 1 atm pressure. Then, as we continue to heat, the temperature of the liquid begins to rise until it begins to boil only at 100 ˚C at 1 atm and produces steam. Thus, the temperature remains constant at the melting point or the boiling point until the less stable phase is completely converted to the more stable phase. Thus, we witness solid to the liquid phase transition of the pure substance at its normal melting point, and then liquid to vapor phase transition at its normal boiling point. We remind ourselves that such phase changes, liquid to vapor, for example, are induced in the functioning of a modern steam turbine or the steam engine of the bygone era, practically driving the recent industrial revolution. Thus, these discussions are of paramount financial, cultural, historical, and commercial importance.

What happens to the chemical potential as we carry out these transformations? When we change the temperature of the system, why is the liquid more stable above the melting point while the vapor is more stable than the liquid above the boiling point? We begin answering by examining the chemical potential of the pure substance as a function of temperature at constant pressure. Later, we will examine the chemical potential as a function of pressure at a constant temperature.

19.3.1 Chemical potential of a phase as a function of temperature

We'll restrict our discussions to pure substances in this chapter, and in this section, we keep the pressure constant. Since Gibbs free energy is a function of pressure and temperature, given by the following relation, we examine its temperature dependence after setting dp =0.

$$dG = V\,dp - S\,dT$$

$$d\mu = \bar{V}\,dp - \bar{S}\,dT$$

In the above equation, the bar over the symbol indicates molar quantities or values divided by the corresponding mole numbers on both sides of the equation. We remind ourselves that the chemical potential (μ) is molar free energy or G/n. Thus, we get the familiar relationship between the chemical potential and the molar entropy from the above equation, at constant pressure, as follows:

$$\left(\frac{\partial \mu}{\partial T}\right)_p = -\bar{S}$$

Therefore, a plot of chemical potential as a function of temperature should give a line (Figure 19.1) with a negative slope equal to the molar entropy of the phase.

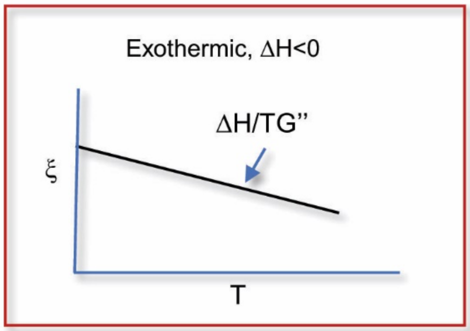


Figure 19.1 Plot of the chemical potential of a pure phase as a function of temperature at constant pressure. The slope is negative and has a value of the molar entropy of the phase. The linear plot is justified only when the temperature range is small because entropy itself is a function of temperature.

The plot is linear, only when we consider a small temperature interval on the x-axis, because the slope, molar entropy, is a function of temperature, and we recognize that the slope will change over a broader temperature range and the plot will not be linear. The third law tells us that the molar entropy of a substance is always positive and hence, the negative slope tells us that the chemical potential of the phase decreases as we raise the temperature. The molar entropy of the phase, therefore, plays a critical role in our discussions of phase transitions. Next, we will examine the pressure dependence of the chemical potential of a phase.

Example 19.1

At constant pressure, what is the rate of change of chemical potential with temperature, if the molar entropy of a substance is 159.9 J/K mol at room temperature?

$$d\mu = -\bar{S}\, dT \text{ when } dp = 0, or \left(\frac{\partial \mu}{\partial T}\right)_p = -\bar{S} = 159.9 \frac{J}{Kmol}$$

19.3.2 Chemical potential of a phase as a function of pressure

Pressure is another variable that we can control in the laboratory to adjust the chemical potential of a system. Similar to the temperature dependence, we now examine the chemical potential at constant temperature (dT =0) using a similar approach. The equation relating the change in the chemical potential with pressure and temperature is recalled and the condition that dT =0 is imposed. Then rearranging the quantities, we get the rate of change of chemical potential with pressure as equal to the molar volume.

$$d\mu = \bar{V}\, dp - \bar{S}\, dT = \bar{V}\, dp$$

$$\left(\frac{\partial \mu}{\partial p}\right)_T = \bar{V}$$

Since volume can’t be negative for any substance, we conclude that the chemical potential should increase with the molar volume of the phase. A plot of chemical potential vs pressure over a short range of pressures gives a straight line with a slope equal to the molar volume at a constant temperature. (Figure 19.2). Since volume itself is a function of pressure, the plot will be non-linear over a wider range of pressures.

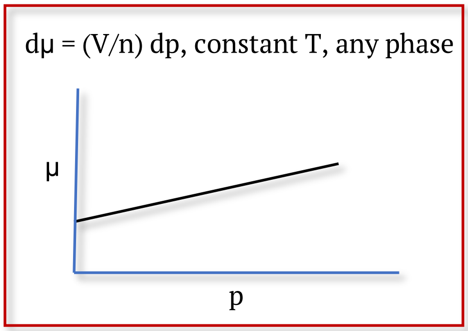


Figure 19.2 Plot of the chemical potential of a pure phase as a function of pressure at a constant temperature. The slope is equal to the molar volume, and hence, it is always positive. Since volume itself is a function of pressure, the plot is linear only over a small range of pressures. It would be non-linear over a wider range of pressures but maintain a positive slope at all points.

Thus, for a single pure phase, over a short range of pressures, we can predict that the chemical potential of a substance increases linearly with pressure, which is not a natural direction. Over a wider range of pressures, it will increase non-linearly or, in fact, exponentially, as we discussed in the previous chapter.

Example 19.2

What is the pressure needed to double the chemical potential of water by applying pressure at 300 K. (molar volume of water at 1 atm, 25˚C is 0.018 L)

$$\left(\frac{\partial \mu}{\partial p}\right)_T = \bar{V} \; or \; \Delta\mu = \left(\frac{V}{n}\right)(p_2 - p_1) \; or \; p_2 = p_1 + \left(\frac{\Delta\mu \, n}{V}\right) = 1 \, atm + \frac{2\frac{J}{mol} * mol}{0.018 \, L} = 112.1 \, atm$$

In summary, the changes in the chemical potential with respect to temperature and pressure are important in the study of phase equilibria. While the increase in temperature lowers the chemical potential of a phase, the increase in pressure raises the chemical potential. These relationships will be of critical value in our next discussion, where we compare the chemical potentials of different phases of a pure substance as a function of temperature or pressure. This step will lead us to the thermodynamics of the phase transitions.

19.4 Chemical Potential and Phases of a Pure Substance at Constant Pressure

Since a phase transition requires more than one phase, how does the chemical potential of one phase of a pure substance compare with that of another phase of the same substance? The motivation is that the phase with the lower chemical potential will be more stable, and the transition from the less stable phase to the more stable phase will be the natural direction.

For a solid, we write the chemical potential as a function of temperature at constant pressure, as stated in the previous discussion, where the molar entropy of the solid ($\bar{S}_{solid}$) is given by the first derivative of chemical potential with respect to temperature.

$$(\partial \mu_{solid}/\partial T)_p = -\bar{S}_{solid}$$

For a liquid, we write the chemical potential as a function of temperature below, where the molar entropy of liquid ($\bar{S}_{liquid}$) is given by the first derivative of chemical potential with respect to temperature.

$$\left(\partial \mu_{liquid}/\partial T\right)_p = -\bar{S}_{liquid}$$

Finally, for the vapor phase, we write the chemical potential as a function of temperature, where the molar entropy of vapor ($\bar{S}_{vapor}$) is given by the first derivative of chemical potential with respect to temperature.

$$\left(\partial \mu_{vapor}/\partial T\right)_p = -\bar{S}_{vapor}$$

A plot of the chemical potentials of the three phases as a function of temperature, at constant pressure, are compared in Figure 19.3. The liquid line is shifted to the right of the solid line, and the vapor line is shifted to the right of the liquid line. This is because solid appears at a lower temperature than the liquid, and liquid appears at a lower temperature than the vapor.

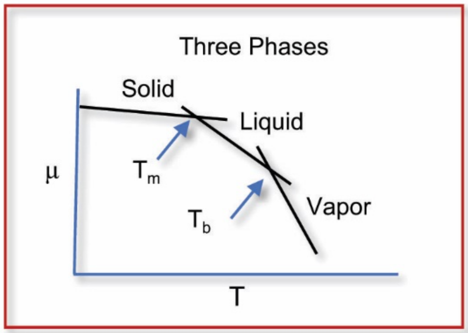


Figure 19.3 Plot of chemical potentials of the solid, liquid, and vapor phases of a pure substance as a function of temperature at constant pressure. The liquid and solid lines intersect at the melting point (T_m) while the liquid and the vapor lines intersect at the boiling point (T_b). The negative slopes are equal to the corresponding molar entropies of the three phases, and the molar entropy of the vapor is greater than that of the liquid, which is greater than that of the solid.

The slopes of all three plots are negative because the chemical potential of any substance decreases with an increase in temperature, as we learned earlier. The third law tells us that the entropy of the vapor is greater than that of the liquid, which in turn is greater than the solid.

$$\bar{S}_{solid} < \bar{S}_{liquid} < \bar{S}_{vapor}$$

Therefore, the liquid line is steeper than that of the solid line and the vapor line is steeper than the liquid line. The solid and liquid lines intersect at the corresponding melting point (T_m) because, at this temperature, the two phases have the same chemical potential and therefore, they are in equilibrium. This is, by definition, the melting temperature of the solid or the freezing temperature of the liquid. If the pressure is held at 1 atm, then this is the normal melting point or normal freezing point of the substance.

From the above expression, we also recognize that the molar entropy of the vapor is larger than the liquid, and the vapor line is steeper than that of the liquid line. The vapor and liquid lines intersect at the corresponding boiling point (T_b) because at this temperature, the two phases have the same chemical potential, and are, therefore, in equilibrium. This is, by definition, the boiling temperature of the liquid. If the pressure is held at 1 atm, then this is the normal boiling point of the substance.

If we start heating a pure solid sample, raise the temperature from left to right, the chemical potential of the solid keeps decreasing along that line, and when the intersection is reached between the solid and the liquid, the solid will spontaneously convert to the liquid. That is because, at the intersection point, both the liquid and solid have the same chemical potentials, like ice-water mixture. There is an equilibrium between ice and water, and they can move either forward or reverse, depending on whether we supply or withdraw heat, which is a reversible process.

If we try to raise the temperature beyond T_m, all the solid will be converted to the liquid before the temperature can be raised above T_m due to this equilibrium. The equilibrium will tend to shift to offset the additional heat being added to the system, which we learned in the previous chapter, until all solid is converted to liquid. We recognize that as the melting of the solid to the liquid.

If we keep heating the liquid along the temperature axis further up, the chemical potential keeps decreasing and we reach the second intersection point T_b. At this temperature, the vapor has the same chemical potential as the liquid and the liquid is at equilibrium with the vapor, and we refer to T_b as the boiling point. If we continue to supply heat, all the liquid would be eventually converted to vapor. Above the boiling point, the vapor has a lower chemical potential than the liquid and the transition from liquid to vapor is spontaneous. Thus, only the vapor phase exists above the boiling point.

In summary, the chemical potentials of the three phases are such that an increase in temperature lowers the chemical potentials in proportion to the molar entropies of the phases. Since the molar entropy of a liquid is greater than that of the solid, the plots of chemical potential vs temperature intersect at the melting point. Similarly, the molar entropy of the vapor is greater than the liquid and the plots of chemical potential vs temperature for these two phases intersect at the boiling point. Thus, the temperature dependence of the chemical potential explains the phase transition temperatures and their natural directions. Next, we examine the three phase transitions in more detail: solid to liquid (melting), liquid to vapor (boiling), and solid to vapor (sublimation).

19.4.1 Solid-liquid equilibrium at constant pressure

Plots of the chemical potentials of the solid and the liquid as a function of temperature are compared in Figure 19.4. The liquid line (green) has a higher negative slope than the solid line (blue) because the liquid phase has a higher molar entropy than the corresponding solid phase. The intersection of these lines is the melting point as discussed earlier.

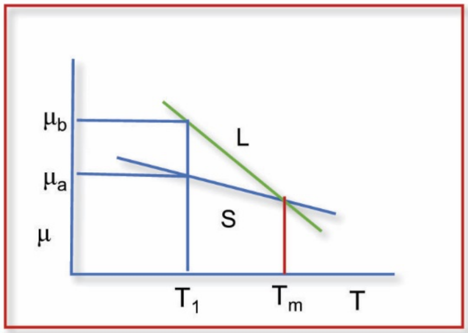


Figure 19.4 Plot of chemical potentials of the solid and liquid phases of a pure substance as a function of temperature at constant pressure.

The liquid and solid lines intersect at the melting point (T_m). The negative slopes are equal to the corresponding molar entropies of the phases, but the third law tells us that the molar entropy of the liquid is greater than that of the solid. Hence, the liquid line is steeper than that of the solid line. An interesting consequence is that the liquid line is placed above the solid line, below the melting temperature. However, the liquid line is below the solid line, above the melting temperature. Solid is more stable below the melting point, while liquid is more stable above the melting point.

If we change the temperature to a higher or a lower value from T_m, we will induce a phase change from one phase to another. For example, at a temperature below T_m, the chemical potential of the liquid (μ_a) is greater than the chemical potential of the solid (μ_b). Thus, below the melting temperature, the solid is more stable than the liquid and we predict that at this temperature, the solid should form spontaneously from the liquid. Thus, we observe in the winters of North America that liquid water freezes below the ice point, spontaneously.

Above T_m, the liquid has a lower chemical potential than the solid (Figure 19.4), and we note that the solid melts spontaneously to form the corresponding liquid. Thus, in the Spring of North America, snow melts spontaneously to liquid water when the winter thaw begins.

19.4.2 Vapor-liquid equilibrium at constant pressure

Let's look at the vapor-liquid equilibrium, just as we looked at the liquid-solid equilibrium. If we start at a high temperature where only the vapor is present and lower the temperature gradually, what do we predict? Plots of the corresponding chemical potentials, as a function of temperature, are given in Figure 19.5, with the intersection point being the boiling point (T_b). At this temperature, liquid and vapor have the same chemical potential and the two phases are in equilibrium.

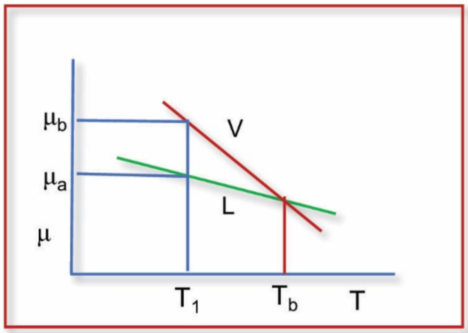


Figure 19.5 Plot of chemical potentials of the liquid and vapor phases of a pure substance, as a function of temperature at constant pressure. At temperature T_1, the vapor has a higher chemical potential (μ_a) than the liquid (μ_b), and hence, the vapor condenses spontaneously to form liquid to lower the chemical potential of the system.

At temperature T_1 (which is below T_b) the liquid has lower chemical potential than the vapor, and the vapor condenses spontaneously to the liquid. This is a natural process we witness, as in the case of rain (Figure 19.6), where the vapor is cooled in the clouds of the upper atmosphere to form water droplets, which grow and begin to fall to the ground as rain.

Figure 19.6 Below the boiling point T_b, the vapor condenses spontaneously to form rain (liquid) from the vapors in the upper atmosphere. When the temperature in the upper atmosphere is too cold, snow may be the result of the freezing of liquid water to solid form (Free stock).

Above the boiling point, the vapor has a lower chemical potential than the liquid, and the liquid boils off spontaneously. This process has occurred long ago on the planet Mars and there appears to be no liquid water on its surface, currently.

19.4.3 Solid-Vapor Equilibrium at Constant Pressure

The equilibrium between the solid and vapor is less obvious in our immediate surroundings, even though specific examples can be cited. Plots of the chemical potentials of the solid and that of its vapor are compared in Figure 19.7. The two plots intersect at the sublimation point (T_s), and at this temperature, solid and vapor have the same chemical potentials and are in equilibrium. This situation is created at low pressures for the sublimation of volatile solids.

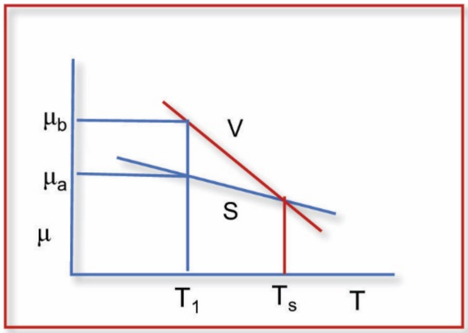


Figure 19.7 Plot of chemical potentials of the solid and vapor phases of a pure substance, as a function of temperature, at constant pressure. At temperature T_1, the vapor has a higher chemical potential (μ_a) than the solid (μ_b), and hence, vapor freezes spontaneously to form a solid and lowers the chemical potential of the system.

At a temperature T_1, below T_s, the vapor has a higher chemical potential than the solid, and it spontaneously converts to the solid without passing through the liquid phase (Figure 19.8). Above the sublimation point, though, the vapor is more stable than the solid and the solid evaporates. Most perfumes are designed such that they sublime slowly at room temperature and pressure, releasing the perfume molecules into the room, gradually. The perfume industry, again, is another multi-billion-dollar industry.

Figure 19.8 Below the sublimation point T_s, the water vapor freezes spontaneously in the upper atmosphere to form snow (solid) without passing through the liquid phase. The picture shows this phase transition happening during one of the Connecticut winters.

In summary, we have discussed the thermodynamic stabilities of substances in terms of their pure phases and the propensities for spontaneous phase transitions between any two of these pure phases. The identity of the most stable phase depends on the temperature at constant pressure, and the phase with the lowest chemical potential is the most stable at a given pressure and temperature.

19.5 Chemical Potentials of Phases and Pressure dependence

So far, we have examined the effect of temperature on the chemical potential of a phase and the temperatures of the phase transitions. Since chemical potential also depends on the pressure, we can ask how are the phase transitions influenced by the pressure? As usual, we keep the temperature constant, examine the influence of pressure on the chemical potential, and evaluate the phase transitions. We recall the pressure dependence of chemical potential as the following, at constant temperature (dT =0).

$$d\mu = \bar{V}\,dp - \bar{S}\,dT = \bar{V}\,dp$$

$$\left(\frac{\partial \mu}{\partial p}\right)_T = \bar{V}$$

We recognize that the rate of change of chemical potential with pressure is equal to the molar volume of the phase, as we saw before, and the molar volumes of the three phases are as follows, with few exceptions:

$$\bar{V}_{solid} < \bar{V}_{liquid} < \bar{V}_{vapor}$$

The molar volume of the solid is less than that of the liquid which in turn is less than the vapor for a given substance, except for water and silicon. In the latter cases, under a narrow set of conditions, the molar volume of the liquid is less than that of the solid. Thus, for most substances, the chemical potential of the solid phase increases with pressure, and the value of the above first derivative increases from solid to liquid to vapor. Now, we use these quantitative relations to consider the effect of pressure on the phase equilibrium.

19.5.1 Phase changes with pressure at a constant temperature

Contrary to the common misconception, phase transitions can be induced by pressure changes at a constant temperature. Since the application of pressure increases the chemical potential of a given phase, we can induce phase transitions with pressure, even when the temperature is kept constant. We can use the μ vs T plot that we discussed in the previous section for the three phases and ask what the effect of pressure will be on these plots (Figure 19.9).

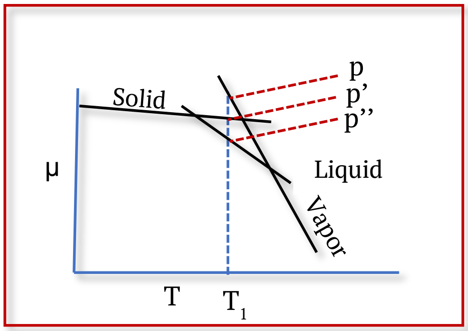


Figure 19.9 Plot of chemical potentials of the solid, liquid, and vapor phases of a pure substance as a function of temperature at constant pressure. The plots are shifted to the right as expected and feature increasing negative slopes, as discussed before. At pressure p" and temperature T_1, the most stable phase is the liquid. When the pressure is increased to p', the solid is formed at the same temperature. When the pressure is raised further to p, the vapor is formed, as illustrated.

If we begin with the liquid phase at temperature T_1 and pressure p", and raise the pressure to p', the chemical potential rises to that of the solid, where the liquid solidifies, spontaneously. Further increase of pressure to p, raises the chemical potential to that of the vapor, and solid sublimes spontaneously, all transitions happening at the same temperature but different pressures. Thus, phase transitions can be induced by changing the pressure at an appropriate temperature and shift the melting, boiling, or sublimation points rationally. Next, as an extension of this discussion, we will examine the effect of pressure on the solid-liquid equilibrium.

19.5.2 Effect of pressure on the melting point

Consider the chemical potentials of the solid and liquid phases of a pure substance as a function of temperature at constant pressure, which we already examined (Figure 19.10, solid lines). When the pressure is decreased from p to p', the chemical potentials of both the phases decrease at all the temperatures, and hence, both the curves are shifted downwards (Figure 19.10, dotted lines).

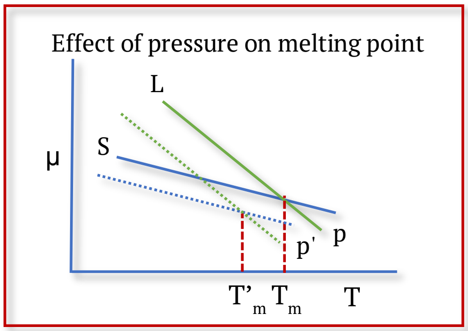


Figure 19.10 Plot of chemical potentials of the solid and liquid phases of a pure substance, as a function of temperature at constant pressure (solid lines). The effect of a decrease in pressure from p to p' on the chemical potentials of the phases (dotted lines) for most substances is shown.

At pressure p, the solid and the liquid lines cross at the melting temperature T_m and when the pressure is decreased to p', the intersection point moves to the left, not to the right. This is because of two reasons. One is that the decrease in the chemical potential of the phase is proportional to the molar volume, and because liquids have larger molar volume than the corresponding solids, their chemical potentials will decrease greater than the corresponding solids. Thus, the liquid line drops much more than the solid line. The second reason is that both lines have negative slopes, as discussed earlier, and hence, in total, a downward shift of the lines with negative slopes moves the intersection points to the left or lower temperatures. Consequently, the melting points decrease with a decrease in pressure for most solid phases.

Ice is one exception. Ice is special because the molar volume of ice is larger than the molar volume of the liquid water at the same temperature and an increase in pressure decreases the melting point of ice. This makes skating on ice possible (discussed below).

19.5.3 Effect of pressure on the boiling point

Consider the chemical potential vs the temperature plot for the liquid-vapor system, as we discussed earlier (Figure 19.11). The red line corresponds to the vapor and the green line corresponds to the liquid. These lines cross at temperature T_b, the boiling point. As we lower the pressure from p to p', the chemical potential of the liquid and the vapor decrease, and both curves are shifted down. The vapor curve is shifted down more than the liquid curve because the molar volume of the vapor is greater than the corresponding solid.

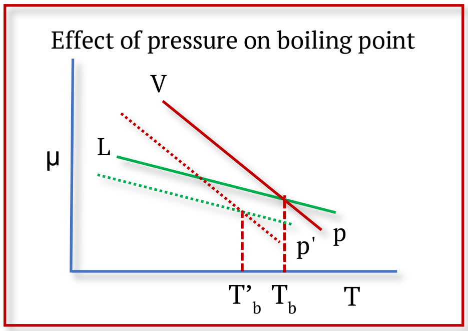


Figure 19.11 Plot of chemical potentials of the liquid and vapor phases of a pure substance, as a function of temperature at constant pressure (solid lines). The effect of a decrease in the pressure from p to p' on the chemical potentials of the two phases (dotted lines) is shown by the dotted lines.

Thus, a decrease in the boiling point is realized because decreased pressure decreases the chemical potentials of both phases, that of vapor more than the liquid. This phenomenon is used in vacuum distillations to lower the boiling points of liquids so that they could be distilled at lower temperatures. To the contrary, an increase in pressure increases the chemical potential, increases the boiling point, increase in boiling point decreases the cooking temperature in a pressure cooker, which in turn hastens cooking. The latter is because the rates of most chemical reactions increase with an increase in temperature.

19.5.3 Effect of pressure on the sublimation point

We will now look at another example of a phase transition, solid to vapor, which is sublimation. Sublimation is the spontaneous conversion of a slid to vapor without ever passing through a liquid phase. This is often observed by lowering the pressure on the system. The effect of reducing the pressure on the chemical potential as a function of temperature is shown in Figure 19.12. The solid line (blue) and the vapor line (red) cross at the sublimation point (T_s). The vapor line has a higher slope because the molar volume of vapor is greater than that of the solid or the liquid. When the pressure is reduced to a certain point, the vapor line falls below the liquid line, and vapor crosses the solid line well below the liquid line. Thus, at T_s, the vapor and the solid have the same chemical potentials and both have lower chemical potentials than the corresponding liquid, at the same temperature.

Normally, the vapor line is on to the right of the liquid line. Its position depends on the pressure because the change in the pressure changes the relative positions of these lines, and the vapor line is much more sensitive to pressure than the liquid or the solid, due to its higher molar volume. So, by lowering the pressure we can lower the vapor line well below the liquid line, and substances can sublime from solid to vapor, directly.

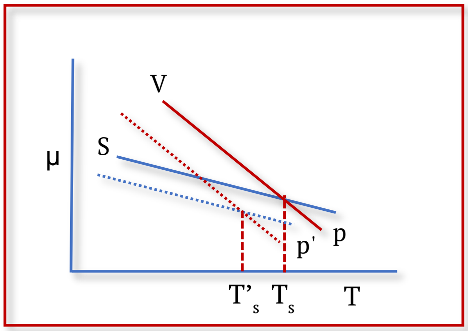


Figure 19.12 Effect of pressure on the sublimation point of a solid. A decrease in pressure from p to p' decreases the sublimation temperature from T_s to T'_s (dotted lines).

Several organic compounds exhibit this kind of property, and they can be sublimed above room temperature, under sufficiently low-pressure conditions (Figure 19.12). We want to lower the sublimation point for a given substance so that it can be sublimed without thermally decomposing. A decrease in pressure lowers the chemical potentials of the solid (blue line) and the vapor (red line), but the vapor line drops much more than the solid, which is due to greater molar volume of the vapor than the solid, and the sublimation point drops from T_s to T'_s.

Figure 19.13 Ferrocene crystals purified by sublimation with a cold finger in a sublimation apparatus, under a high vacuum (from Wikipedia).

This phenomenon is useful for the purification of solids, just like boiling is a simple way to purify volatile liquids by distilling them. The picture in Figure 19.13 shows ferrocene crystals that have been purified by sublimation onto a cold finger. The outer vessel (not shown) contains the substance to be purified, the inner jacket (shown) has a cooling system where the sublimed sample condenses, and the whole thing is evacuated to control the pressure as desired. This phenomenon of sublimation is also exploited in the fragrance industry so that you can have vapors of fragrance under atmospheric conditions without ever converting the solid to the liquid form. Camphor, for example, evaporates at room temperature. Dry ice (solid carbon dioxide) also evaporates directly from the solid phase.

In summary, we looked at the effect of pressure on phase transitions by relating it to the effect of pressure on the chemical potentials. The melting point, boiling point, or sublimation point of a substance can be lowered by decreasing the pressure. This is due to the decrease in chemical potential as we decrease pressure, and the extent of the decrease depends on the molar volume of the corresponding phase. These influences are important in many processes in the laboratory industry, as well as in our daily lives.

19.6 Clapeyron Equation

The Clapeyron equation describes, quantitatively, the effect of pressure on the phase transition temperatures and relates to the entropy and volume changes accompanying the phase transitions. We can then make quantitative predictions of changes in the transition temperatures.

Let there be any two phases α and β in equilibrium, such that the chemical potential of phase α at temperature T and pressure p equals to the chemical potential of the phase β at the same temperature and pressure. An ice-water mixture in a wine glass is an example of two phases in equilibrium and the chemical potential of the ice at zero degrees Centigrade and one atmosphere is exactly equal to the chemical potential of water under the same conditions.

$$\mu_\alpha\,(T,p) = \mu_\beta\,(T,p)$$

Let there be a change in the pressure of the system by dp so that the phase transition temperature changes by dT. The system moves in response to this change in pressure, and at the new equilibrium, the chemical potentials of the phases are equal again.

$$\mu_\alpha\,(T+dT,p+dp) = \mu_\beta\,(T+\,dT,p+dp)$$

Chemical potentials of the two phases are given in terms of molar volume and molar entropy terms as follows:

$$d\mu_\alpha = \bar{V}_\alpha\,dp - \bar{S}_\alpha\,dT$$

$$d\mu_\beta = \bar{V}_\beta\,dp - \bar{S}_\beta\,dT$$

Because the two phases are in equilibrium, we write these two terms being equal and then group the volume and entropy terms.

$$\bar{V}_\alpha\,dp - \bar{S}_\alpha\,dT = \bar{V}_\beta\,dp - \bar{S}_\beta\,dT$$

$$\left(\bar{V}_\alpha - \bar{V}_\beta\right)dp = \left(\bar{S}_\alpha - \bar{S}_\beta\right)dT$$

We write the rate of change of pressure with respect to the phase transition temperature (T) as below, and this is the famous Clapeyron equation:

$$\frac{dp}{dT} = \frac{\Delta\bar{S}}{\Delta\bar{V}}$$

The rate of change in pressure with respect to the phase transition temperature is directly related to the change in the molar entropy and inversely related to the change in molar volume. A plot of pressure vs the phase transition temperature is shown in Figure 19.14, and the slope of the line is the ratio of change in entropy to change in volume accompanying the phase transition.

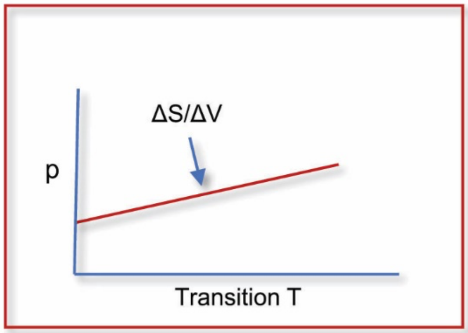


Figure 19.14 Effect of pressure on the phase transition temperature. The slope of the line is positive for most substances and is given by the Clapeyron equation.

The plot is linear over a small temperature interval, but the slope is positive for most substances. The change in phase from solid to liquid, for example, has positive values for both ΔS and ΔV, and the slope is positive. Thus, an increase in pressure increases the phase transition temperature, for most substances, except for ice-water equilibrium. This latter result is because ΔS for ice to the water phase transition is positive but ΔV of ice to water is negative. So, water is the exception to the rule. For all other substances, the slope is positive, and the plot is a straight line over a short temperature interval. Thus, by integration of the Clapeyron equation, we can relate the phase transition temperature at one pressure to another pressure, as described below.

Example 19.3

At 0 ˚C, the molar volume of ice is 0.0196 L and that of water is 0.018 L, the molar entropy for melting of ice is 22.1 J/K mol. What is the change in the melting temperature with unit pressure increase?

$$\frac{dp}{dT} = \frac{\Delta\bar{S}}{\Delta\bar{V}} \ or\ \Delta T = \Delta p * \frac{\Delta V}{\Delta S} = 1\ atm * \frac{(0.018 - 0.0196)L\ K\ mol}{22.1\ J\ mol} * \frac{101.3\ J}{L\ atm} = -0.0073\ K$$

19.7 Heats of Phase Transitions

Since the Clapeyron equation is written for the phase equilibrium, we replace ΔS with ΔH/T and write the following for solid to the liquid phase transition. The phase transition temperature is in the denominator.

$$\frac{dp}{dT} = \frac{\Delta H_{fusion}}{T_m\ \Delta V_{fusion}}$$

Thus, the heat of fusion (ΔH_{fusion}) and the change in the volume due to fusion (ΔV_{fusion}) are intrinsically related to the phase transition temperature. For liquid-vapor and solid-vapor phase transitions, we can write similar equations, as below.

$$\frac{dp}{dT} = \frac{\Delta H_{vaporization}}{T_b\ \Delta V_{vaporization}}$$

$$\frac{dp}{dT} = \frac{\Delta H_{sublimation}}{T_s\ \Delta V_{sublimation}}$$

We have already discussed how pressure raises the chemical potentials of substances and why the phase transition temperatures increase with pressure, in general. By studying the transition temperature as a function of pressure, we can estimate the ratio of ΔH/ΔV for the transition, and if we know one of these quantities, the other can be obtained.

For example, the ΔH for fusion, evaporation, or sublimation is >0 because the conversion of solid to liquid, or liquid to vapor, requires overcoming intermolecular forces. It takes energy to melt a solid to form the liquid and the liquid requires energy to form the vapor, for all substances.

Example 19.4

What is the decrease in the boiling point of water in the city of Denver, CO; at an elevation of 5,280 feet it is considered the mile-high city, from the boiling point at the sea level?

The normal barometric pressure in the City of Denver is 615 mm Hg, and heat of vaporization of water is 40.8 kJ/mol and change in volume on evaporation is 30.6 L at 100 ˚C. Neglecting the effect of temperature on the enthalpy and volume changes due to small decrease in the boiling point, we get the following:

$$\frac{dp}{dT} = \frac{\Delta H_{vaporization}}{T_b\ \Delta V_{vaporization}} \ or\ \Delta T = \Delta p \left(\frac{T_b\ \Delta V_{vaporization}}{\Delta H_{vaporization}}\right)$$

$$= \left(\frac{(760 - 615)\ mm\ Hg * atm * 101.315\ J}{760\ mm\ Hg * atm\ L}\right)\left(\frac{373.15\ K\ mol * 30.6\ L}{40.8\ kJ}\right) = -5.4\ K$$

Thus, cooking in this city would need extra time to boil unless a pressure cooker is used to compensate for the drop in pressure with altitude.

In most cases, except for water, ΔV >0 because the liquid occupies more volume than the solid, and the vapor occupies more volume than the liquid or the solid. The slope of the plot of pressure vs the transition temperature is linear over a short range of pressure with a positive slope. But both ΔH and ΔV are functions of pressure and temperature, and hence, the plot of pressure vs the transition temperature over a wider range of pressures is a curve, but the slope at each point on this curve is positive (Figure 19.15).

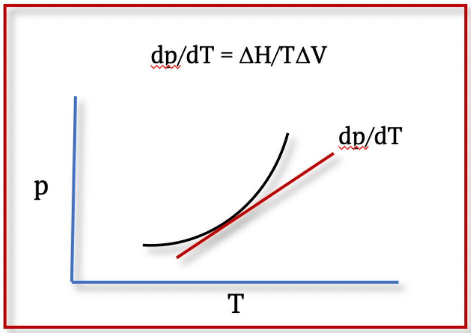


Figure 19.15 Effect of pressure on the phase transition temperatures over a wide pressure range. The slope of the line at each point is positive for most substances and is given by the Clapeyron equation.

We notice an upward curvature for the plot, and that is because the slope is a function of ΔV, which dominates the value of the slope. This is because the molar volume of the gas is much larger than that of the solid or the liquid and an increase in temperature increases the molar volume of the gas more rapidly than that of the solid or the liquid. So, the slope of the plot is always positive and increases with temperature. If we increase pressure, the phase transition temperature increases as well. We also note that the slope depends on ΔH. But ΔH is only weakly dependent on temperature while ΔV depends on temperature more strongly and ΔV is in the denominator. Thus, the net effect of raising pressure is that the phase transition temperature increases, and the slope of the plot increases. This scenario is applied to condensed phase-gas equilibria for most substances. The case of the solid-liquid equilibrium is discussed next.

19.8 Solid – Liquid Equilibria

For the equilibrium between the solid in contact with the liquid at its melting point, the plot of pressure versus melting temperature describes how the melting point depends on pressure. Clapeyron equation tells us that the plot will depend on the entropy and volume changes, and we write these quantities, explicitly, as follows:

$$\Delta\bar{S} = \bar{S}_{liquid} - \bar{S}_{solid} > 0$$

$$\Delta\bar{V} = \bar{V}_{liquid} - \bar{V}_{solid} > 0$$

The change in the molar entropy will be greater than zero because the third law tells us that the liquid will have greater entropy than the solid. Similarly, the change in molar volume will be >0 for most substances, because the liquid usually has a larger volume than the solid due to some unoccupied space present in the liquid. Thus, the slope of the plot of p vs the phase transition temperature (T) given by the Clapeyron equation is written as follows, in terms of these variables:

$$\frac{dp}{dT} = \frac{\Delta\bar{S}}{\Delta\bar{V}} = \frac{\Delta S}{\Delta V} = \frac{\Delta H}{T\,\Delta V}$$

The plot of p vs transition temperature for the solid-liquid equilibrium (Figure 19.16) has a positive slope because both ΔH and ΔV are positive for most solid-liquid transitions, some enthalpy needs to be supplied to melt the solid, and ΔV is positive as most liquids occupy more space than solids.

$$\frac{dp}{dT} > 0$$

The plot is linear over a narrow range of pressures but may curve over a wider range of pressures for the reasons discussed earlier.

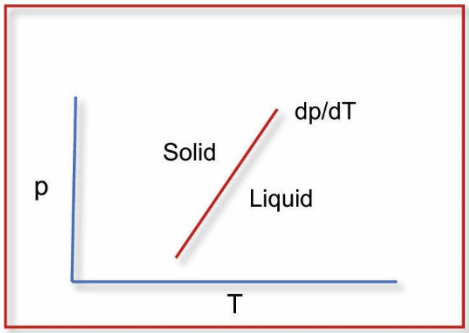


Figure 19.16 Effect of pressure on the phase transition temperature of solid-liquid equilibrium for most substances.

19.8.1 Integration of the Clapeyron Equation for Solid-Liquid Equilibria

Integration of the Clapeyron equation provides a simple relation to calculate the phase transition temperature at any pressure when its value is known at one pressure. The integrated equation will be applied to estimate the heats of vaporization, sublimation, and fusion by non-calorimetric methods, which is very useful for practical applications.

The Clapeyron equation given below is re-arranged with the pressure terms on one side and the temperature terms on the other, as follows:

$$\frac{dp}{dT} = \frac{\Delta H_{fusion}}{T_m\,\Delta V_{fusion}}$$

$$\int_1^2 dp = \int_1^2 \frac{\Delta H}{\Delta V}\frac{dT}{T}$$

Both ΔH and ΔV are temperature dependent, and we assume that over a small temperature interval and for solid-liquid equilibria, we treat them as constants. Integration with limiting states 1 and 2 gives us the relation we are seeking, directly, as follows:

$$p_2 - p_1 = \frac{\Delta H_{fusion}}{\Delta V}\ln\left(\frac{T_2}{T_1}\right)$$

Rearranging, we obtain the change in the phase transition temperature (ΔT) in terms of ΔH and ΔV for solid-liquid transition, or fusion of the solid as follows:

$$\ln\left(\frac{T_2}{T_1}\right) = \ln\left(\frac{T_1 + T_2 - T_1}{T_1}\right) = \ln\left(1 + \frac{\Delta T}{T_1}\right) \sim \frac{\Delta T}{T_1}$$

$$\Delta p \sim \frac{\Delta H_{fusion}\,\Delta T}{\Delta V_{fusion}\,T_1}$$

So, by measuring ΔT as a function of Δp for the solid-liquid phase transition, and by measuring ΔV value, one can calculate ΔH_{fusion} by a non-calorimetric method. By knowing the constants and the phase transition temperature at one pressure, we calculate the phase transition temperature at another pressure.

Example 19.5

Calculate the decrease in the melting temperature of a solid when the pressure is reduced by half.

Let the melting temperature of the solid be T_m at 1 atm and T'_m at 0.5 atm, the difference in the molar volumes of the liquid and the solid be ΔV, and the decrease in the melting temperature be $\Delta T = T'_m - T_m$.

$$\Delta p = 0.5\ atm \sim \frac{\Delta H_{fusion}\,\Delta T}{\Delta V_{fusion}\,T_m}$$

We conclude that $\Delta T = 0.5\ \text{atm} * T_m * \Delta V/\Delta H$.

19.9 Pressure Dependence of Gas-Condensed Phase Equilibria

By supplying heat, we can convert solid to the vapor (sublimation, at reduced pressure) or liquid to the vapor (boiling or evaporation) and we are interested in the heats of these phase transitions. Writing the Clapeyron equation for the solid-gas equilibrium, we get the following, in terms of heat of sublimation ($\Delta H_{\text{sublimation}}$) and volume change ($\Delta V_{\text{sublimation}}$).

$$\frac{dp}{dT} = \frac{\Delta H_{sublimation}}{T_s \, \Delta V_{sublimation}}$$

We recognize that the volume change will be largely due to the production of the gas phase from the condensed phase, and we need to write the volume change in terms of temperature or pressure. Thus, we first invoke a reasonable approximation that the volume change will be essentially equal to the volume of the gas itself, produced during the transition. Therefore, we write $\Delta V = V_{\text{gas}}$. For example, one mole of ice or water has a volume of ~18 mL, give or take a few mL, and upon conversion to vapor, it will occupy nearly 22.4 L at one atmosphere and 0 ˚C. Thus, the molar volume of ice is negligible when compared to the molar volume of the water vapor. Thus, we can justify this approximation.

$$\Delta V = V\ (gas) - V\ (solid) \sim V\ (gas)$$

Now, we recognize that the temperature dependence of Vgas is not negligible, and we can proceed to integrate only if we express it in terms of temperature or pressure. Here, we make the second approximation that gas behaves ideally, and use the ideal gas law.

$$(gas) = n\,R\,T/p$$

After substituting these into the Clapeyron equation, we integrate between the limits pressure 1 atm at To and pressure of p atm at temperature T.

$$\int_1^p \frac{dp}{p} = \int_{T_0}^{T} \frac{\Delta H\, dT}{n\,R\,T.T}$$

Thus, we obtain the logarithmic expression connecting pressure with ΔH for the solid-vapor or liquid-vapor phase equilibrium.

$$\ln p = -\frac{\Delta H}{n\,R}\left(\frac{1}{T} - \frac{1}{T_0}\right)$$

Example 19.6

Calculate ΔH when the vapor pressure in equilibrium with a liquid increases from 24 to 760 mm Hg as the temperature increases from room temperature to 100 ˚C.

$$\ln p = -\frac{\Delta H}{n\,R}\left(\frac{1}{T} - \frac{1}{T_0}\right)$$

$$\Delta H = -nR\ln\left(\frac{p_2}{p_1}\right)\left(\frac{TT_0}{T_0 - T}\right) = -1\,mol\ R\ \ln\left(\frac{760}{24}\right)\left(\frac{(100-25)K}{298.15\ K * 373.15\ K}\right) = 42.61\ kJ/mol$$

Some important comments to be kept in mind are that we are assuming that ΔH is a constant over this temperature and pressure range, and this is reasonably accurate for most substances but could deviate over a wider range of temperature or pressure. Then, we need to express it in terms of temperature as well. If the gas (real gases) does not behave ideally, we express gas volume using the corresponding equation of state and then carry out the integration. Thus, one needs to pay attention to the integration step and choose the strategy appropriately.

The third important comment is that we chose the lower limit for pressure to be 1 atm, and this is convenient for experimental measurements in the laboratory. By using the ratio of pressures, the pressure units cancel. Thus, we have a convenient experimental method to get the phase transition temperatures at different pressures.

The plot of ln(p) versus 1/T is a line with a slope equal to -ΔH/nR (Figure 19.17). The slope of the plot depends on the sign of ΔH, and ΔH is positive for condensed phase to gas transition.

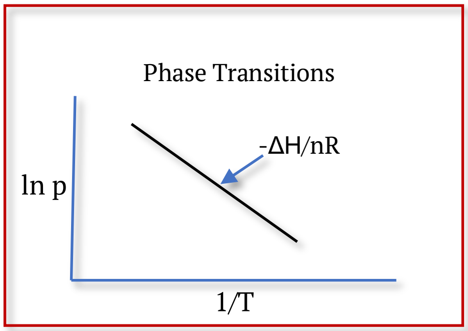


Figure 19.17 Plot of pressure vs 1/T for the gas-solid or the gas-liquid transition temperature, for most substances, giving a slope equal to -ΔH/nR.

In the laboratory, we measure vapor pressure versus temperature for a liquid-gas transition or solid-gas transition, and from the plot, we can obtain the enthalpy of the phase transition without using a calorimeter. Thus, a non-calorimetric method of measuring the enthalpy of vaporization or enthalpy of sublimation is obtained, and this is often used in the undergraduate physical chemistry laboratory.

In summary, we have integrated the Clapeyron equation for three different cases, two of which are analogous. We assumed that ΔH is constant in all cases, and this is probably accurate over a small range of pressures but the temperature dependence of ΔV is to be treated more carefully. When the gas phase is one of the two phases, then we use ideal gas law to write the volume change in terms of temperature, before integration. We conclude that the slope of the line gives ΔH for the phase transition under investigation.

19.10 Molecular Interpretation

Chemical potential successfully predicts the melting point, boiling point, and sublimation points of a pure substance, and explains the effect of pressure on these phase transitions. A phase transition occurs spontaneously to lower the chemical potential of the system. During the melting of a pure solid to a liquid, for example, the cohesive energy of the solid is overcome by the thermal energy of the system and the particles break free of each other's attractive forces. The transition is sharp or happens at a constant temperature (melting point) because the extra heat supplied is used to liberate more and more particles from the solid to the liquid phase until all the solid phase is converted to the liquid phase. Thus, during the melting point, the solid, and liquid are in equilibrium and the temperature remains constant.

Thus, supplying heat during a phase transition shifts the equilibrium toward the more stable phase, while the temperature remains constant until the transition is complete. The transition, thus, is highly cooperative or occurs in a narrow temperature range. Since all particles are held at about the same strength of the cohesive force (pure, single phase), all particles undergo the transition over a narrow temperature range. Thus, these transitions are very sharp for pure substances. The converse is true when we lower the temperature and allow the vapor to condense to the liquid or allow the liquid to freeze to a solid. One can conclude that phase transition temperatures are characteristic of the intermolecular forces between the particles.

The Clapeyron equation provides an experimental method to estimate the heats of these transitions, and the heat supplied to convert a more stable phase to a less stable one is a measure of the inter-particle forces described above. Thus, one supplies enthalpy to overcome these forces and one concludes that the enthalpy of the liquid is greater than the solid and that of the vapor is greater than that of the condensed phases.

Thus, the excess energy supplied for the phase transition is stored in terms of the potential and kinetic energies of the particles. The energy is stored in various degrees of freedom of the particles as well as the intermolecular potentials. One can then guess that particles that have fewer degrees of freedom will have lower enthalpies of phase transitions, and this is directly related to the number of atoms present in the molecule. As the number of atoms in a molecule increases, so does the number of degrees of freedom. In addition, the amount of energy stored in these degrees of freedom also depends on the strengths of bonds connecting the atoms in the molecule. Weaker bonds have vibrational spacings closer than stronger bonds.

Hence, more vibrational and associated rotational or translational states are available for storage of this energy for weaker bonds. Thus, substances that have weaker bonds will have lower enthalpies for phase transitions than substances that have stronger bonds, in general.

Another important insight is that hydrogen bonding between molecules enhances the intermolecular forces and holds the particles together tightly. Thus, condensed phases that have hydrogen bonding have higher enthalpies of phase transitions than the ones that lack these interactions. Along these lines, ionic substances have higher enthalpies of phase transitions due to the strong cohesive forces between the particles, and metals also have high enthalpies of transitions due to the strong metallic bonds between the constituent particles. Thus, one can understand the physical basis for the phase transitions and enthalpies of transitions at the atomic and molecular levels.

19.11 Applications in daily Life

Elevation of the boiling point of water with an increase in pressure is used in a pressure cooker, which is a practical device in the kitchen. By this trick, we raise the temperature of the food contents to a higher temperature than the normal boiling point of water. Normally, food is cooked at 100 ˚C, the normal boiling point of water, but by increasing pressure to 15 to 17 pounds per square inch (psi), the boiling point of water can be raised to ~120 ˚C. Thus, water inside the pressure cooker boils at a higher temperature than at room temperature, and thus, the contents cook much faster. Remember, every 10 ˚C increase in temperature doubles the rates of most reactions. So, by raising the temperature by 20 ˚C above the normal boiling point, cooking time could be reduced by a quarter. That is the reason food cooks much faster with a pressure cooker. Conversely, water boils at a lower temperature on mountain tops and foods need to be cooked longer. In a turbine, the steam pressure is raised to high values, thus raising the temperature of the boiler, the steam and the boiling point, so that a greater amount of work can be extracted from the higher-pressure steam at higher temperatures. The higher the temperature differential, the greater the efficiency of the Carnot engine, and this engine drove the industrial revolution, literally.

Solids with strong cohesive forces, such as titanium and diamond, have some of the highest melting points. Pure titanium was used to make the canopy of the stealth reconnaissance aircraft of the US Airforce SR71. The canopy of this aircraft exceeded temperatures of 300 ˚C during its flight at three times the velocity of sound. Thus, because of high melting point of titanium, the aircraft canopy does not soften or melt at the cruising speed of the aircraft.

19.12 Key points

1. Chemical potential is an important concept in chemistry, and among other things, it is a function of pressure and temperature. An increase in temperature decreases chemical potential, while the increase in pressure increases it.
2. The natural phase transitions that we witness around us are driven by a decrease in chemical potential, and they stop when no further decrease in μ is possible. This change is controlled by both the molar volume and molar entropy terms of the two phases because chemical potential is a function of these variables.
3. At the phase transition, $\Delta\mu = 0$, at constant temperature and pressure because the phases are at equilibrium at the transition temperature.
4. For most substances, the transition temperature decreases with a decrease in p or increases with an increase in p.
5. The change in the transition temperature as a function of pressure, depends on the differences in the molar entropies and molar volumes of the phases.
6. The ice point decreases with an increase in pressure, one of the few exceptions, and this makes skating possible. The increase in pressure due to the person's weight and the narrow width of the skate blade melts a small layer of ice into water and the skater glides with ease. This same effect is also at play when we slip on black ice in the winter unless we are very careful. On the other hand, we cannot skate on dry ice because its melting point does not decrease with an increase in pressure, the melting increases instead.
7. Using the Clapeyron equation, the enthalpies of phase transitions can be measured by a non-calorimetric method.

19.13 New terms and units

Molar volume, molar entropy, and chemical potential, Clapeyron equation, phase transition temperature, heats of phase transitions, and volumes and entropies of phase transitions.

$$\left(\frac{\partial \mu}{\partial T}\right)_p = -\bar{S}$$

$$\left(\frac{\partial \mu}{\partial p}\right)_T = \bar{V}$$

$$\frac{dp}{dT} = \frac{\Delta \bar{S}}{\Delta \bar{V}}$$

$$\frac{dp}{dT} = \frac{\Delta H_{fusion}}{T_m \, \Delta V_{fusion}}$$

$$\Delta p \sim \frac{\Delta H_{fusion} \, \Delta T}{\Delta V_{fusion} \, T_1}$$

$$\ln p = -\frac{\Delta H}{n\,R}\left(\frac{1}{T} - \frac{1}{T_0}\right)$$

19.14 Self Reflection

1. In the space of your dorm room, list different phase transitions taking place in a 24 cycle, 30-day cycle, and one year cycle.
2. Assume you are hiking in the mountains at a height of about 1.5 miles. You plan to make dinner by cooking some dry beans and veggies, but you know the boiling point of water decreases with height. How would you overcome this issue using your knowledge of Physical Chemistry?
3. You wish to integrate the Clapeyron equation, but you only know ∆V but remember Trouton's rule. How would you proceed?
4. Imagine that you are hiking over Mount Washington in the northeast, during early spring. What phase transitions you might encounter during your hike on this mountain?
5. How would you explain to your 5-year-old nephew why a sheet of ice becomes slippery around its melting point but not well below that temperature?
6. How would you explain to your grandma (even if she knows) how the unique properties of water make skating possible?
7. Plot G vs p at constant T, G vs T at constant p, and show changes in μ for sublimation, boiling, and melting transitions.
8. Explain why dry ice (solid CO_2) sublimes but does not melt under room temperature conditions. Use μ vs T plots to articulate your explanation, not the phase diagram.
9. When you look at pictures of Mount Everest or other tall mountains, you see a white glaze on one side of the mountain. Not all photos have this, but many do. What is this haziness due to?
10. How would you explain to your 5-year-old brother how is rain formed in the upper atmosphere, using the principles of phase transitions? Hail formation on a summer afternoon, but not in winter?

19.15 Further Reading

1. https://ocw.mit.edu/courses/chemistry/5-60-thermodynamics-kinetics-spring-2008/video-lectures/lecture-18-phase-equilibria-2014-one-component/2.https://ocw.mit.edu/courses/chemistry/5-111-principles-of-chemical-science-fall-2008/video-lectures/lecture-18/13.6
2. https://ocw.mit.edu/courses/materials-science-and-engineering/3-012-fundamentals-of-materials-science-fall-2005/lecture-notes/lec15t.pdf
3. https://ocw.mit.edu/courses/materials-science-and-engineering/3-012-fundamentals-of-materials-science-fall-2005/lecture-notes/lec10t.pdf

19.16 Self Tests

1. The key thermodynamic variable that describes the spontaneity of the phase transition behavior is

  a. enthalpy
  b. entropy
  c. chemical potential
  d. internal energy
  e. none of these

2. Clapeyron equation connects these key variables:
   a. the phase transition temperature with ΔS and ΔH of a chemical reaction
   b. the phase transition temperature with ΔS and ΔV of a chemical reaction
   c. the phase transition temperature with ΔS and ΔV of the phase transition
   d. the phase transition pressure with ΔS and ΔH of the phase transition
   e. none of these
3. The enthalpies of phase transitions are indicative of
   a. intermolecular volume
   b. intermolecular distances
   c. intermolecular interactions
   d. molecular velocities
   e. none of these
4. The chemical potential of a pure phase
   a. increases with temperature, at constant pressure
   b. decreases with temperature, at constant pressure
   c. decreases with increase in pressure, at constant temperature
   d. increases with pressure and temperature
   e. none of these
5. The chemical potential of a pure phase
   a. increases with temperature, at constant pressure
   b. decreases with pressure, at constant temperature
   c. increases with pressure, at constant temperature
   d. increases with pressure and increase in temperature
   e. none of these
6. The following is an example of a phase transition:
   a. boiling of water
   b. chemical reaction in progress
   c. stone rolling down the hill
   d. both a and b
   e. none of these
7. The phase transition temperature is
   a. the temperature when one phase disappears and another appears
   b. the temperature when one phase is in equilibrium with another
   c. the temperature when two phases merge into one
   d. The temperature when only one phase exists
   e. none of these
8. When one phase is converted to another, spontaneously, the following decreases
   a. chemical potential of the system
   b. enthalpy of the system
   c. entropy of the system and the surroundings
   d. both a and c
   e. all of the above
9. Slope of the plot of chemical potential on the y-axis and temperature on the x-axis at constant pressure, for a pure phase is
   a. >0
   b. <0
   c. =0
   d. can't say
   e. none of these
10. Slope of the plot of chemical potential on the y-axis and pressure on the x-axis for a pure phase, at constant temperature, is

a. molar volume
b. <0
c. =0
d. molar entropy
e. none of these

11. Plots of the chemical potentials of pure solid and liquid phases, as a function of temperature, at constant pressure, intersect at
a. the boiling point
b. freezing point
c. sublimation point
d. infinity
e. none of these

12. In general, the molar entropy of a pure liquid is
a. greater than the vapor but less than the solid
b. greater than that of the corresponding solid but less than molar entropy of the vapor
c. greater than that of the corresponding vapor but less than the molar entropy of the solid
d. smaller than that of the corresponding solid but more than the molar entropy of the vapor
e. none of these

13. For the vapor and solid phases of a pure substance to be in equilibrium, their
a. masses should be the same
b. volumes should be the same
c. heats should be the same
d. their entropies should be the same
e. none of these

14. The rate of change of chemical potential with respect to pressure at constant temperature is
a. molar entropy
b. molar enthalpy
c. molar volume
d. molar free energy
e. none of these

15. The chemical potential of a pure phase
a. increases with pressure at constant temperature
b. decreases with pressure at constant volume
c. increases with mole numbers
d. decreases with pressure at constant temperature
e. none of these

16. The boiling point of a pure liquid increases with
a. increase in mole numbers
b. increases with molar volume
c. decrease in pressure
d. increase in pressure
e. none of these

17. The ratio of change in the molar entropies to change in molar volumes of two pure phases is 3 kcal /(L K). The rate of change of the phase transition temperature with respect to pressure of the two phases is
a. 3 LK/kcal
b. 0.3 LK/kcal
c. 9 LK/kcal
d. (1/3) LK/kcal
e. none of these

18. The ratio of the molar heat of sublimation to molar change in volume for two pure phases in equilibrium at 0 ˚C is 15 kcal/L. The rate of change of the sublimation temperature with pressure is
a. 15 L/kcal
b. (1/15) L/kcal
c. (1/15) kcal/L
d. can't say
e. none of these

19. The ratio of the enthalpy of fusion to volume of fusion for a pure substance is 10 J/L at 10 ˚C. The change in pressure needed to raise the fusion temperature from 10 ˚C to 20 ˚C is
    a. 10 J/L
    b. 0.82 atm
    c. 0.82 J/L
    d. 10000 Pa
    e. none of these
20. The molar enthalpy of sublimation of a pure solid at 1 atm and 300 K is 8.31 J/mol. The value of ln(pressure) needed to lower the sublimation point to 150 K is
    a. 1/300
    b. 1/290
    c. (1/300) K
    d. –(1/300)
    e. none of these

19.17 Self Tests Key

1. c, 2. c, 3. c, 4. b, 5. c, 6. a, 7. b, 8. d, 9. b, 10. a, 11. b, 12. b, 13. e, 14. c, 15. a, 16. d, 17. d, 18. e, 19. e, 20. d

19.18 Problems

1. The ratio of change in the molar entropies to change in molar volumes of two pure phases is 3 kcal /(L K). The rate of change of the phase transition temperature with respect to the pressure of the two phases is (Ans. 0.0081 K/atm)
2. The ratio of the molar heat of sublimation to molar change in volume for two pure phases in equilibrium at 0 ˚C is 15 kcal/L. The rate of change of the sublimation temperature with pressure is (Ans. 2.20 K/atm)
3. The ratio of the enthalpy of fusion to the volume of fusion for a pure substance is 5 kJ/L at 10 ˚C. The change in pressure needed to raise the fusion temperature from 10 ˚C to 20 ˚C is (Ans. 1.74 atm)
4. The molar enthalpy of sublimation of a pure solid at 1 atm and 300 K is 8.31 J/mol. The value of pressure needed to lower the sublimation point to 150 K is (Ans. 0.9966 atm)
5. The vapor pressure of ethanol changes from 44 torr to 760 torr when heated from room temperature to its boiling point. What is its molar heat of vaporization? (Ans. 34.06 kJ/mol)
6. For ethanol, molar standard entropy is 159.9 J/K mol. What is its change in chemical potential when it is heated from room temperature to its boiling point? (Ans. -8.47 kJ/mol)
7. What is the increase in the chemical potential of water when it is pressured to 100 atm under ambient conditions? (Ans. 180/5 J/mol)
8. What is the pressure required to lower the melting temperature of ice by one kelvin? Based on this result, explain why the 2-mile-thick ice sheet of Greenland does not drift away. (Ans. 136.3 atm)
9. Most pressure cookers generate a pressure of 15 psi inside the container, with respect to outside pressure. What is the boiling point of water if the cooker is used at the sea level? (Ans. 128.9 ˚C)
10. Use the calorimetric data and equilibrium concept to explain why water evaporates spontaneously at room temperature, well below its boiling point.

Chapter 20. The Phase Rule

After completing this chapter, you will be able to:

- Recognize the number of components degrees of freedom and the number of phases.
- Construct the phase diagrams of water and CO_2 and be able to predict the phase behavior.
- Design methods to apply the phase rule to control chemical equilibria

Goals

- Define phase, components, constituents, degree of freedom, and the phase rule.
- Examine the p vs T plots of the phase transitions of substances, using water and carbon dioxide.
- Apply the phase rule to chemical equilibria to predict the composition of the reaction mixtures under equilibrium
- Devise strategies on how to drive the equilibrium in a desirable direction.

20.1 Why study this?

Discussions of the last chapter, lead us naturally into the discussions of the phase diagrams of pure substances. Phase rule summarizes phase diagrams and phase diagrams are relevant to the laboratory studies and relevant to our daily life experiences. For example, weather forecasting depends heavily on phase diagrams because they are announcing the timing of various phase transitions of the important fluid, water, on this planet! The phase diagrams are critical for engineering and industrial applications as well. Phase diagrams of alloys and other substances, for example, are of great significance in preparing advanced materials for high technology applications. Phase diagrams predict the equilibrium compositions of chemical reactions over a wide range of experimental conditions and, therefore, are of high significance in industrial chemistry.

Phase diagram of water, for example, is of importance for terrestrial and outer planetary missions where water may exist under extremely high pressures and temperatures or extremely low temperatures and low pressures. Rain, snow, and water evaporation from the ocean surface are all very important phase transitions that are intricately entangled with our weather, as well as climate change. Phase diagrams are also useful in controlling chemical equilibria, with a high impact on the industrial production of chemicals. Phase diagrams are also important for the fundamental understanding of physical chemistry. At the molecular level, the phase transitions tell us how the intermolecular forces play out these transitions and provide a different viewpoint at the atomic forces. Thus, phase diagrams document what phases exist under a given set of pressure, temperature, and reaction conditions, which are relevant to our daily lives, practical applications, and fundamental chemistry. Thus, a study of this chapter familiarizes us with phase transitions happening around us and tailors our technological/daily needs.

20.2 Phase Rule

Phase rule relates the number of phases, number of components, and degrees of freedom of the system. For example, the temperature is a degree of freedom and pressure is another degree of freedom. If there is more than one substance in the system, then the composition is another degree of freedom. When we have a system consisting of certain compositions and a certain number of phases, then we would like to know how many ways the system can be prepared to get unique states from it. When we have ice and water in equilibrium, for example, at 1 atm and 0˚C, we ask if we can vary the temperature or raise the pressure without disrupting the solid-liquid-vapor equilibrium. Can we vary both these degrees of freedom at the same time? These are the kinds of questions that are addressed by the phase rule. Moving along these lines, we examine the definitions of key terms of this chapter and then examine the phase rule itself.

20.2.1 Definitions of phases, components, and the degrees of freedom

Phase is a physically uniform substance that is continuous with distinct physical boundaries such that we can identify its presence and distinguish it from other phases of the system. For example, ice, water, and vapor are distinct phases that can be readily identified, and their physical boundaries assessed. This does not imply that a phase must be pure; it has to be physically uniform and continuous. For example, a solution of water and salt is a single phase, even though it has both salt and water distributed intimately, uniformly, and continuously. If there is excess salt that is not dissolved in the solution, then salt is a distinct phase in contact with its solution. Thus, a phase need not be pure. Graphene, diamond, water, steam, etc., are phases whose boundaries can be established and their presence observed.

The definition of components, or the chemical constituents, is important for our discussions. For example, chemically distinct species such as water, oxygen, nitrogen are all different chemical components of a system, regardless of which phase they are present in. Salt-water solution without any vapor above it, for example, is a single phase with two distinct chemical constituents. Thus, the phase of a substance and the number of chemical constituents in it are separate entities.

A clear distinction between the chemical constituents and components is to be made. The number of components is defined as the minimum number of chemical species needed to define all the chemical constituents of the system. The number of components need not be equal to the number of chemical constituents. Take the following example:

Example 20.1

Ammonia is produced from nitrogen and hydrogen from an equilibrium reaction mixture of hydrogen and nitrogen in the presence of a catalyst. Here, we have three different constituents, ammonia, hydrogen, and nitrogen, but we don't need all three substances to define the system.

This is because the equilibrium concentrations of any two of these chemical constituents define the concentration of the third constituent via the equilibrium constant. Thus, we only need the concentrations of two of the chemical constituents and, therefore, the number of components is 2, not 3. Since chemical equilibria have finite compositions at defined temperature and pressure for each chemical equilibrium, we have one less component than the number of chemical constituents. When the three chemical constituents of the ammonia synthesis are not in equilibrium, we need the concentrations of all three substances, and in that case, the number of components will be equal to the number of chemical constituents.

The number of degrees of freedom is the number of independent variables such as temperature, pressure, and the number of mole fractions of specific chemical constituents that are needed to define the entire system completely. Again, we keep in mind that each chemical equilibrium will reduce the number of components by one. The phase rule relates the number of components and phases with the degrees of freedom of a system. Few examples follow to further clarify these definitions.

20.2.2 Single component systems

When we have a pure substance, we have a single chemical constituent and a single component. It may exist in one or more phases, under certain conditions of temperature and pressure. If there is only liquid water with no vapor in equilibrium, then it is a single component, single phase system. A tank of hydrogen gas is another example of a single phase of a single component system. You can pressurize the tank to different pressures at different temperatures until another phase of hydrogen appears. A single component system is not limited to a single phase. When we have a single phase, we can vary either temperature or pressure, and thus, the system has two degrees of freedom.

Normally, liquid water has vapor in equilibrium with it (2 phases), and both phases can exist at various temperatures and pressures, and the system has one degree of freedom. That is, when we fix the temperature, the vapor pressure is automatically fixed due to the liquid-vapor equilibrium. The equilibrium provides an equation restricting the chemical potential of the liquid to be equal to the chemical potential of the vapor.

When we heat liquid water to reach its boiling point at 1 atm pressure, we still have two phases in equilibrium and the system has a fixed boiling point. But this can be varied if desired and water can still boil at different temperatures, depending on the pressure above it. Thus, one component, two-phase system has only one degree of freedom.

Example 20.2

Consider a three-phase system of ice, water, and vapor. Cooling of water, at 1 atm external pressure, for example, begins to freeze to the ice at 0 ˚C. At this temperature, liquid, vapor, and the solid, all three phases, can co-exist. The system has no degrees of freedom. If we change temperature or pressure, one of the three phases will disappear. So, one component, three-phase system has zero degrees of freedom, and it is the triple point. Thus, the number of phases restricts the number of degrees of freedom, with each phase decreasing the degree of freedom by 1.

20.2.3 Multicomponent systems

In a multi-component system, we have multiple chemical constituents and hence we have the composition as an additional degree of freedom, which increases the number of ways that the system can be chosen. By adding a second component, for example, we need to define the mole fraction of at least one component, then the mole fraction of the other component is automatically fixed because the two mole fractions should add up to one. Thus, with an additional component, we have an additional degree of freedom to prepare the system in addition to pressure and temperature. Thus, the degrees of freedom increase with the number of components, but all mole fractions need to sum to zero, providing one additional restriction on the increased degrees of freedom.

Consider a system of one phase and C components. We need to define C-1 mole fractions to fix its composition completely, and it still can have pressure and temperature as the independent degrees of freedom. Then we can say the number of degrees of freedom (F) has (C-1) compositions, in addition to pressure and temperature as the degrees of freedom.

20.2.4 System of P-phases

Each additional phase restricts the degrees of freedom due to the equilibrium between them. That is one equation of chemical potentials is generated for each phase equilibrium. If there are 2 phases in equilibrium, the chemical potential of one phase must equal the other and the degree of freedom is reduced by one. That is, when the chemical potentials of the two phases are equal, we can only change pressure or temperature. Changing one fixes the value of the other to keep the equilibrium intact. Thus, a system of P phases in equilibrium will have its degrees of freedom reduced by P-1.

Example 20.3

For example, at the triple point of pure water, where three phases are in equilibrium, the degrees of freedom are reduced by 3-1 or by 2. Neither pressure nor temperature can be changed. If we change either of these, then one of the phases will disappear.

20.2.5 General formula: System of C-components and P-phases

While each component increases the degrees of freedom by C-1, each phase reduces it by P-1, but pressure and temperature are the standard degrees of freedom. This way we can determine the total number of degrees of freedom (F) for a system of C components and P phases as follows:

$$F = (C - 1) - (P - 1) + 2$$
$$F = C - P + 2$$

This equation is the famous Phase Rule, and we will apply this rule in the examples below to deduce the number of degrees of freedom the system has. This is useful to study how the phase behavior changes as we add or subtract components or change the pressure or temperature on the system. This scenario is summarized for a few systems in Table 20.1.

Table 20.1. The components, phases, and degrees of freedom allowed for a system.

	Components	*Phases*	*Degrees of freedom*
1	1	1	2
2	1	2	1
3	1	3	0
4	2	1	3
5	2	2	2
6	2	3	1

In summary, the allowed degrees of freedom increase with increasing the number of components because the system can have a certain number of mole fractions to be defined, while the phase equilibria reduce these degrees of freedom due to the restriction that the phases that are in equilibrium should have the same chemical potentials.

20.3 Phase Diagrams and the Application of the Phase Rule

When we examine large ranges of pressure or temperature, new phases might appear, in addition to the solid, liquid, and vapor. These could be allotropes of solid phases. Thus, phase diagrams are constructed from experimental measurements to document what phases exist under what conditions, and the window of the pressure and temperature axes shown in the diagram depend on the available experimental data. Usually, the solid phase dominates at the lower temperature and the vapor persists at higher temperatures, while the liquid is wedged in between, and other solid phases might appear at very high pressures or supercritical phases may appear at high pressures and temperatures. At most of the temperatures and pressures, most substances have multiple phases, and these diagrams are generally referred to as phase diagrams. In this chapter, two examples are discussed: carbon dioxide and water.

20.4 Phase diagram of CO_2

The phase diagram of carbon dioxide (Figure 20.1) describes the effect of pressure on the phase transition temperatures between various possible phases of this substance. This has only one constituent and one component and hence the number of degrees of freedom depend on the number of phases present at the specific temperature and pressure values.

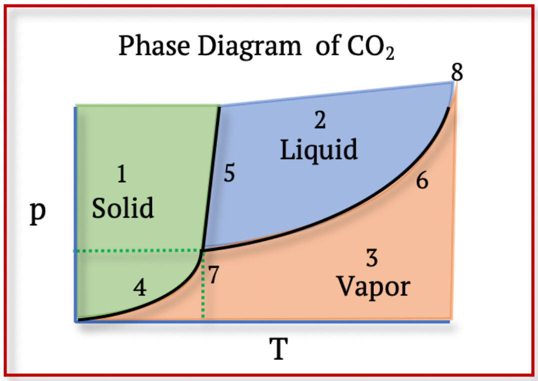


Figure 20.1 Plot of pressure vs temperature for the phase equilibria of carbon dioxide over a limited range of pressures and temperatures (phase diagram). Three distinct regions (green, blue, and orange) are identified, where a single phase exists (marked 1, 2, and 3, as examples). Each line describes the equilibrium between two phases, and each point on the line represents the equilibrium pressures/temperatures (marked 4, 5, and 6 as examples), while the intersection point of the three lines (marked 7) shows the equilibrium between three phases at one pressure and temperature. The liquid and vapor phases merge into one at and above the critical pressure and temperature (marked 8).

20.4.1 One component and one phase (regions)

The phase diagram is divided into specific regions, marked as solid (green), liquid (blue), and vapor (orange) but there could be other allotropes of the solid phase when the pressure-temperature window is widened but these are not shown here for simplicity. Each area is demarcated by line boundaries and represents one phase.

For a one-component, one-phase system, the Phase rule gives two degrees of freedom (F = (1-1) -(1-1) +2=2). For any given pressure, the region gives an infinite number of temperature values where the system can exist. Thus, one can vary either the temperature or the pressure independently, and hence the system has two degrees of freedom. The green, blue, and orange areas represent these regions of pure phases That is, only one phase (marked 1, 2, and 3) exists in each of these three areas, and each phase has two degrees of freedom.

20.4.2 One component but two phases (lines)

Each line on the diagram (Figure 20.1) represents the co-existence of two phases in equilibrium. For each pressure, there is a corresponding specific temperature of the phase equilibrium defined by the line. Thus, according to the Phase rule, there is just one degree of freedom for the system (F = (1-1) -(2-1) +2 = 1). The phase equilibrium is disrupted when we go out of this set of pressure-temperature values, and one of the phases disappears. Thus, we have a solid-liquid line, solid-vapor line, and liquid-vapor line, the three distinct equilibria of which we are normally familiar with.

As we move along the solid-vapor line, the solid and the gas are in equilibrium, and the liquid phase does not exist under these conditions. The line ends at 5.1 atm and 56.7 ˚C for carbon dioxide. Thus, if we heat the solid present at any point on this line, it directly gets into the vapor phase, or if we cool the vapor present at any of these points, it directly gets into the solid phase without passing through the liquid phase. These conditions represent the range over which sublimation of carbon dioxide occurs, discussed earlier. Thus, if we need to sublime the solid, we simply choose the right pressure and temperature from the phase diagram to ensure that it passes directly from the solid to the vapor, without the appearance of the liquid. For this reason, solid carbon dioxide is converted to gas at room pressure and temperature, the solid is referred to as the dry ice, and the liquid phase does not occur under standard laboratory conditions.

Example 20.4

What is the slope of the solid-vapor line for CO_2 phase diagram?

The slope is dp/dT where p is the applied pressure and T is the transition temperature. This is given by the equation from the last chapter as following:

$$\frac{dp}{dT} = \frac{\Delta\bar{S}}{\Delta\bar{V}} = \frac{51.1\,J}{K\,mol} * \frac{mol}{22.4\,L} * \frac{L\,atm}{101.325\,J} = 0.023\,atm/K$$

The molar entropy of sublimation is 51.1 J/K mol and volume of sublimation is 22.4 L at STP, and substitution of these values, we get the slope of the solid-vapor line as shown above to be 0.023 atm/K.

As we move along the solid-liquid line, we can convert solid to liquid or liquid to solid by choosing the pressure or the temperature from the phase diagram. At the pressures and temperatures defined by this line, the vapor phase does not exist. The liquid-vapor line is at the junction of these two regions of the phases and represents the series of equilibrium conditions for these to co-exist. Note that the slope of this line is greater than zero. This is true for almost all substances, except water (discussed below). The negative slope of the line is quantified by the Clapeyron equation as equal to ΔS/ΔV, as discussed in the last chapter. As we move along this line, we only have one degree of freedom. We can change the temperature, or we can change the pressure to keep the phase equilibrium, but not both.

Example 20.5

What is the slope of the solid-liquid line in the phase diagram of carbon dioxide? (molar entropy of fusion = 40 J/K mol and molar volume of fusion -0.0016 L/mol)

$$\frac{dp}{dT} = \frac{\Delta\bar{S}}{\Delta\bar{V}} = \frac{40\,J}{K\,mol} * \frac{mol}{-0.0016\,L} * \frac{L\,atm}{101.325\,J} = -246.7\,atm/K$$

Note that the liquid-vapor line ends abruptly above a certain temperature (31 ˚C) and pressure (56.7 atm), and only one phase exists at and above this point, which is discussed next. This is referred to as the critical point at which the substance acquires some of the properties of liquid as well as the vapor, and it is referred to as the critical fluid. The critical point is where the liquid and gas have no phase boundary and the critical point for carbon dioxide is at 31 ˚C and 72.9 atm. The thermal energy is no longer able to hold the particles in the liquid phase, yet the interparticle interactions are still strong enough to behave like a liquid. The supercritical carbon dioxide, the phase at this temperature, has interesting properties which make it suitable for removing caffeine from coffee beans, washing clothes without a surfactant, and numerous other industrial applications.

20.4.3 One component but three phases (single point)

The third aspect is the intersection of the three lines. The three phase boundaries meet at a single point where the three phases co-exist at a specific set of pressure and temperature (triple point). Here, the system has no degrees of freedom (F = (1-1) – (3-1) + 2 = 0) and the triple point for carbon dioxide is at -56.7 ˚C and 5.1 atm. At this point, the liquid carbon dioxide, the gas, and the solid are all in equilibrium, and by changing the pressure or temperature, one or more phases will disappear. The phase diagrams of most substances resemble that of carbon dioxide, but water is special, which is considered next.

20.5 Phase diagram of water

The phase diagram of water has demarcation lines among the three-phase equilibria, labeled as the ice, water, and vapor, just as any other substance. The ice-vapor line describes the series of equilibria where the solid will sublime directly into vapor. The slope is defined by the ratio of ∆S and ∆V for the transition from ice to vapor. Both these quantities are positive and hence, the slope is positive. Since liquid water does not exist under these conditions, these conditions are used for freeze-drying of aqueous solutions and suspensions. Samples are first frozen under one of these conditions and ice is allowed to evaporate without passing through the liquid phase. Due to the absence of liquid water, molecular aggregation is prevented during the evaporation of the solid solvent, which is important in drying delicate biological molecules. Next, we consider the ice-water line, which is characteristic of water and a few other substances.

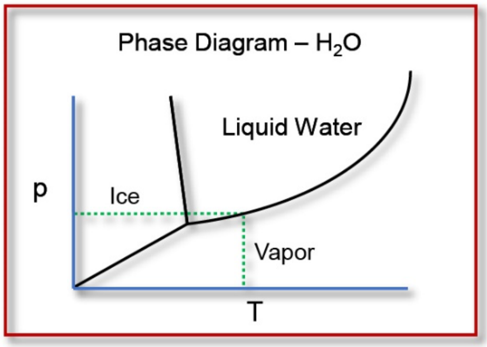


Figure 20.2 Plot of pressure vs temperature for the phase equilibrium of water. Three distinct regions are identified, where each line describes the equilibrium between the two phases while the intersection point shows the equilibrium between all three phases.

The ice-water line has two phases in equilibrium, and the following conditions apply. We have the solid in equilibrium with the liquid water, and it is the plot of pressure vs the melting point of ice defined by the Clapeyron equation.

$$\left(\frac{dp}{dT}\right) = \frac{\Delta S}{\Delta V}$$

Since the volume of ice is greater than the volume of liquid water, the slope is negative for the ice-water equilibrium.

Example 20.6

What is the slope of the solid-liquid line in the phase diagram of water? The molar fusion of ice at 0 ˚C is -0.0016 L/mol, while the enthalpy of fusion is 6.01 kJ/mol.

$$\left(\frac{dp}{dT}\right) = \frac{\Delta S}{\Delta V} = \frac{\Delta H}{\mathrm{T}_m\,\Delta V} = \frac{\left(6010\,\frac{J}{mol}\right) * Latm}{273.15\,K\,(-0.0016)(L/mol)(101.325\,J)} = -131.28\,atm/K$$

The negative slope shows that increase in pressure decreases the melting point of ice. This makes skating possible on the skating rink.

$$\left(\frac{dp}{dT}\right) < 0$$
$$\because S > 0\ and\ \Delta V < 0\ for\ water$$

The negative slope of the line is unusual, and this is because the ratio of ΔS to ΔV is negative, which is due to the larger volume of the solid than the liquid. Thus, if we increase pressure on the ice, the melting temperature decreases. This is the reason skating is possible. This is also the reason water ponds freeze at the top first, while the liquid water remains underneath before the entire pond is frozen solid. Since ice is a good insulator, it slows down the cooling of the liquid water below the ice, and life can continue to thrive in the liquid phase. If $\Delta V>0$, then the ice would be heavier than water and it would sink to the bottom and freeze the lake solid, rapidly. Thus, liquid water supports a myriad of life forms during the winters even when the top is frozen solid. Thus, this anomalous property of water is perhaps another important reason that life flourishes on this planet.

At the liquid-vapor line, we have liquid water in equilibrium with the vapor and the system has one degree of freedom. When the water vapor reaches 1 atm pressure, the corresponding temperature is referred to as the normal boiling point (Figure 20.2, dotted line). From the phase diagram, we can predict the boiling points of water at various pressures. This is useful for desalination, where the temperature required to evaporate water can be reduced by applying vacuum and desalination has immense importance for water purification. The production of pure water from the sea by inexpensive methods is an important problem of the 21st century! The liquid-vapor line ends abruptly, and at this point and above, there is no demarcation between the liquid and the vapor, or it is the critical point (647 K and 221 MPa), which is challenging to achieve in most laboratories.

The ice-vapor line indicates the series of conditions under which ice spontaneously evaporates without forming liquid water. The converse of this process is snowing where the vapor spontaneously solidifies to form a solid, and Figure 20.3 is taken when two feet or more of snow fell in Connecticut in 2016. One can see the snowblower was buried as the amount of snow is nearly knee-deep. These properties of water make it very interesting and responsible for the phenomenon of snowing on this planet. Other planets may have rain, snow, or other substances. When the vapor is condensed to snow, the latent heat of freezing is released into the upper atmosphere, thus warming it up. This is one reason the temperatures are not too cold when it is snowing unless winds in the upper atmosphere transport this heat quickly to other regions.

Figure 20.3 The storm of 2016 in the State of Connecticut that dumped more than two feet of snow in a few hours, which was more than needed to bury the snowblower.

In Figure 20.2, all three lines meet at the triple point where ice, water, and water vapor are in equilibrium, and the system has zero degrees of freedom. The triple point of water is at 0 ˚C and 611 Pa. Below the triple point, ice will directly convert into vapor, or vapor will directly condense into the solid.

Example 20.7

Discuss the change in Gibbs free energy when the water vapor in the upper atmosphere is converted to snow. The surface of the water is heated by the sun and kept warm due to the thick blanket of the atmosphere, while the upper atmosphere transmits most of the sunlight and remains at a lower temperature due to radiative cooling. As warm air rises from the ocean surface to the upper atmosphere, it cools to temperatures well below the triple point of water, and the vapor condenses spontaneously to the solid ice or snow. If the temperature of the atmosphere is warm enough, it falls as rain, but when the temperatures are cold enough, snow reaches the surface of the planet. The conditions on other planets could be such that they might support the raining or snowing of substances such as carbon dioxide or nitrogen, for example

In summary, we recognize that phase diagrams store a lot of information. We examined two specific substances, water, and carbon dioxide, over limited ranges of pressure and temperature. The triple point is important because all three phases (liquid, vapor, and solid) co-exist only under these conditions. Above the critical point, the distinction between liquid and vapor vanishes, and the substance is considered a supercritical fluid. Often, these fluids have unusual properties and are useful for industrial applications.

20.6 Effect of Pressure on Vapor Pressure

One other important aspect of our discussion of phase transitions is the effect of external pressure on the vapor pressure of a liquid. When water evaporates from the ocean surface into the atmosphere, it is under atmospheric pressure, but the atmosphere is not pure water vapor. There are other gases in the atmosphere, and these have a substantial influence on the evaporation of water. For example, increased CO_2 levels in the atmosphere due to the burning of fossil fuels were not considered in estimating its contribution to water evaporation, yet this is important. Here, we will examine how the pressure of inert gas over a liquid influences its evaporation and test if increased CO_2 levels are to be considered to evaluate the increased evaporation of oceans due to climate change.

Example 20.8

The discussion is also important to answer, what would happen if we add inert gas such as CO_2 into the bottle containing a beverage, as in a bottle of a soft drink such as carbonated water. We ask, what would be the vapor pressure after the inert gas is introduced? The answer can be deduced using the fundamental equation of chemical potential and has enormous commercial importance for the beverage and packaging industry.

Consider that we have a liquid and a vapor of a pure substance in equilibrium at temperature T and pressure p, in the initial state. The chemical potential of the vapor equals the chemical potential of the liquid, at the equilibrium temperature and pressure. By introducing the inert gas into the system, above the liquid, we perturb the equilibrium. We ask if the vapor pressure of the liquid would increase or decrease, then by how much?

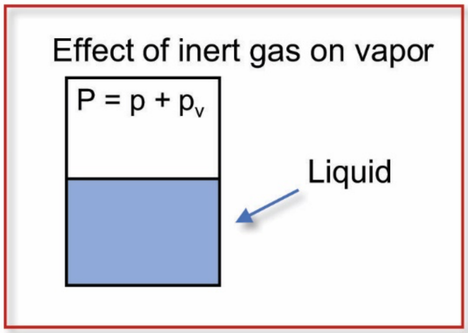


Figure 20.4 Let there be liquid in a container with no gas above the liquid, and then, allow it to evaporate to occupy the remaining volume. This is our initial state. Then, we introduce an inert gas to achieve a total pressure P. The change in vapor pressure due to the addition of the inert gas is deduced below.

The initial state is the liquid in a closed container in equilibrium with pure vapor above it, at pressure p (Figure 20.4). Then, we introduce some amount of inert gas into the vapor phase through a valve and allow it to equilibrate to a final pressure P, including that of any vapor that may have formed or condensed due to the addition of the inert gas. We assume that the inert gas does not react with the liquid or vapor or dissolve in the liquid. It is just inert, and this is our final state.

Our strategy is to write the chemical potentials of the liquid and vapor phases and examine them as a function of applied pressure. Integration of the resulting expression gives us quantitation of how the external pressure influences the vapor pressure of the liquid. Thus, there are two distinct steps to our strategy:

Step 1: We start with the fact that the chemical potentials of the liquid and pure vapor of the corresponding liquid are equal due to the equilibrium between them. We differentiate this equation with respect to the total pressure P at constant T as shown below.

$$\mu(vapor) = \mu(liquid)$$

$$\frac{d\mu_{vapor}}{dp}\frac{dp}{dP} = \frac{d\mu_{liquid}}{dP}$$

We note that the differential is applied in two steps on the right side. One is the derivative of the chemical potential with respect to p, and this is multiplied by the derivative of p with respect to P. That is, we write the rate of change of chemical potential of the vapor with respect to P is equal to a product of two differentials.

$$\frac{d\mu}{dp} = \bar{V}$$

The first term, at constant temperature (dT=0), is simply equal to the molar volume of the vapor. The same is the situation for the liquid phase and the term on the right side of the equation is the molar volume of the liquid, and after the substitution, we get the expression as shown below.

$$\bar{V}_{vapor}\frac{dp}{dP} = \bar{V}_{liquid}$$

Step 2: We proceed to integrate the above, but we realize that the molar volume of the vapor is also a function of pressure and can ignore the change in the molar volume of the liquid. So, we express the molar volume of the vapor in terms of pressure, assuming the ideal gas model.

$$\frac{R\,T}{p}\frac{dp}{dP} = \bar{V}_{liquid}$$

If the vapor does not obey the ideal gas law, we can use a suitable equation of state and express molar volume in terms of pressure, then proceed with integration. We choose the limits po and p, where po is the pressure in the absence of the inert gas, p is the partial pressure in the presence of the applied inert gas. P is the total pressure in the presence of the inert gas, so that p =P-p0, or the change in the vapor pressure due to the application of the inert gas.

$$\int_{p_0}^{p}\frac{R\,T}{p}\,dp = \int_{p_0}^{P}\bar{V}_{liquid}\,dP$$

Integration with these limits gives the final expression as a logarithmic relation, where the ratio of the vapor pressures depends on the total pressure on the liquid.

$$\ln\frac{p}{p_0} = \frac{\bar{V}_{liquid}}{R\,T}\,(\Delta p)$$

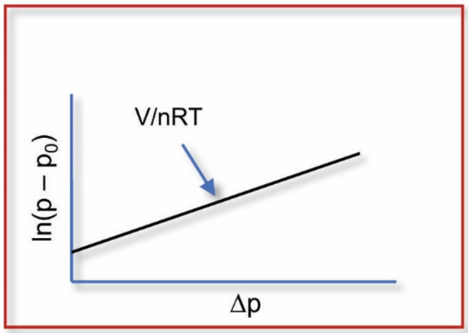


Figure 20.5 Plot of ln(p/p_o) vs Δp for the gas-liquid equilibrium with applied pressure, with a slope equal to V/nRT.

A plot of ln(p/p_0) as a function of P-p_0 gives a straight line with a positive slope equal to the volume of the liquid divided by nRT, where n is the number of moles of the liquid, not the vapor (Figure 20.5). The slope is positive because the molar volume of the liquid, R and T, are all positive quantities.

Example 20.9

Calculate the increase in vapor pressure (∆p) of 5 moles of a volatile liquid of 5 L, when an inert gas is injected into the container at an initial vapor pressure of 1 atm and 350 K and final pressure of 2 atm.

Liquid volume = 5 L. Since 5 moles of liquid occupy this volume, the molar volume is 1 L/mol.

Initial vapor pressure (p0) = 1 atm

Final pressure = 2 atm; ∆p = 1 atm

Substituting in the following relation, we get the final answer:

$$\ln\frac{p}{p_0} = \frac{\bar{V}_{liquid}}{R\,T}\,(\Delta p) = \frac{1(L/mol) * mol\ K}{0.0820\ L\ atm * 350\ K} * 1\ atm = 0.174$$

Since initial vapor pressure is 1 atm, taking antilog gives us a final pressure of 1.19 atm or an increase of vapor pressure by 0.19 atm.

By converting the above logarithmic function to the corresponding exponential function, by taking anti-logarithms on both sides, we recognize that the vapor pressure increases exponentially with a complicated set of terms in the exponent as follows:

$$p = p_0\, e^{\left(\frac{\bar{V}_{liquid}}{R\,T}(\Delta p)\right)}$$

The variable ∆p = (P-p0), or the increase in the vapor pressure due to the application of pressure. When there is no inert gas applied, ∆p =0 and p = p0, one of the limiting conditions. Thus, vapor pressure increases wan ith an increase in inert gas pressure, but the increase is a growing exponential function. The growth function is because V, R, n, and T are all positive.

Example 20.10

When carbon dioxide levels go up in the atmosphere, it acts as the inert gas exerting pressure on the oceans. Then, water vapor pressure should go up exponentially with the partial pressure of carbon dioxide, thus increasing the heat capacity of the atmosphere due to the increased mole fraction of the water vapor in it. Water vapor is one of the worst greenhouse gases and could have a significant impact on climate change. In one of the recent reports of climate change, these simple facts were not taken into account in global warming.

Thus, we conclude that the vapor pressure inside the soda bottle increases exponentially when we raise the pressure above the liquid inside the bottle by injecting CO_2 at a constant temperature. When we open the cap, we see misty vapors of water condensing back due to a decrease in pressure.

In summary, we have looked at the vapor-liquid equilibrium and the vapor pressure increases with applied inert gas pressure, which is of fundamental importance and relevance to climate change and the beverage industry.

20.7 Molecular Interpretation

As described earlier, phase transformations are spontaneous processes driven by differences in chemical potentials. The transitions from solid to liquid, liquid to vapor, or solid to vapor requires intrinsic energy (H) to overcome the forces of attraction between particles, and a certain amount of entropic penalty also applies. We discussed these issues in the previous chapter and all those conditions apply to the contents of this chapter as well. In addition, we need to examine the molecular detail of the critical point and the supercritical state. At the critical point, the adhesion forces between the particles and the thermal energy of the particles are at balance, and, therefore, we predict that critical temperature might provide a good measure of the non-ideal behavior of the gas.

On the other hand, supercritical fluids are in a dilemma as to behave like a liquid or as a gas. Thus, these fluids are dense like liquids due to the strong adhesive forces that are still at work, but the thermal energy is strong enough to disrupt the liquid state, pushing it into the realm of a gas. It is the balance of the opposing terms that make the supercritical fluids very interesting. The weakened intermolecular forces increase the interparticle distances of the liquid particles that create voids, and these fluids have a different dielectric constant, polarity, and viscosity than either the gas or the liquid. Thus, increased interparticle distances are one of the players that make these fluids exhibit unusual properties.

20.8 Applications in Daily Life

Phase diagrams of substances are of importance in daily life, as illustrated by the processes of rain and snow. They are constantly at work in your refrigerator or the freezer, and the number of phases changes as foods is frozen, thawed, or when we boil water to make a cup of tea. Supercritical fluids are finding increasing numbers of applications in the industry. Supercritical CO_2, for example, is used in the decaffeination of coffee beans without losing flavor. Its use for decaffeination is claimed as being a natural way to remove caffeine because they use CO_2 but there is nothing natural about it. Nature does not produce supercritical CO_2, at least not on earth! It is also being used for oil extraction from spent oil wells, purification of delicate pharmaceuticals, and even in the laundry industry. It has this magic ability to pull the dirt out of clothes and then you simply evaporate the supercritical carbon dioxide, only to be recycled to do the next load. This way, dry cleaning is done without using a hydrocarbon solvent, which can pollute the environment.

Supercritical CO_2 is present on the surface of Venus because its atmosphere is composed of >95% CO_2 and the surface temperature and pressure of the planet are above the critical point of this gas. Both gas giants have conditions that are above the critical points of hydrogen and helium, which are their major constituents. Thus, supercritical fluids could be present in many parts of the universe, naturally.

Supercritical water is present naturally in the earth's crust due to high pressures and temperatures that are above its critical point (647 K and 22.1 MPa). It plays an important role in the geology of the crust and has been detected at deep ocean vents called 'black smokers'. Since supercritical water dissolves silicates and minerals as it exits the vents at the ocean floors, the fluid is cooled and the minerals are no longer soluble but precipitate, which gives the strong black color. Supercritical water is a strong oxidant and used for the clean conversion of biomass to a mixture of combustible gases. It is also of high importance for green chemistry industrial applications. Thus, the roles of supercritical fluids are becoming more and more relevant in our daily life, and they are finding increasing numbers of applications.

Freeze drying is important in preparing microporous or nanoporous nanomaterials where normal drying collapses the micropores due to the surface tension forces of the solvent during the evaporation of the liquid solvent. Thus, by freeze-drying, pore-collapse is prevented, and frozen solvent is removed by sublimation to give dry samples with the retention of delicate pore structures.

Desalination is an important problem to be addressed during this century, and the phase diagram of water provides a series of pressures where the liquid can boil to the vapor and the vapor can be condensed to liquid with a low energy penalty. Since phase transitions occur between pure phases, water can be separated from salt by vacuum distillation at a variety of temperatures by adjusting the pressure.

The increase in the surface evaporation of our oceans by the addition of carbon dioxide to the atmosphere from the combustion of fossil fuels may appear small. However, on the scale of the planet and the mass of the total carbon dioxide present in the atmosphere, this increase in heat capacity of the atmosphere due to increased vapor pressure is enormous. Increased concentration of CO_2 increases the surface evaporation of oceans and the resulting increase in humidity further contributes to the greenhouse effect. This increased heat retention and increased global temperature, in turn, can further increase the surface evaporation of water, and so on, in a vicious cycle until the system attains equilibrium. This fact was not taken into account in a recent research report while estimating the effect of increased CO_2 levels in the atmosphere. Water vapor is a very significant greenhouse gas as well.

The effect of inert gas on vapor pressure is illustrated when we uncork a soda bottle. When the pressure is reduced suddenly, the vapor pressure inside the bottle is much greater than it would be at the atmospheric pressure, even if the bottle is brought to room temperature before opening. Of course, the release of pressure over the liquid releases the inert gas dissolved in the liquid as gas bubbles, following Henry's law, which is another phase change. Thus, the bottling company has to be careful to account for the increase in vapor pressure due to added inert gas and design a safe bottle of beverage to be transported to the consumer.

20.9 Key Points

1. Phase transitions are important in chemistry, physics, biology, and in many other disciplines, including important industrial applications.

2. Many phase changes are natural processes that we witness around us, and they are driven by a decrease in chemical potential. They stop when no further decrease in chemical potential is possible.
3. Clapeyron equation relates the effect of pressure on the phase transition temperature via the changes in the molar entropies and molar volumes of the phases involved.
4. Integration of the Clapeyron equation provides a simple method to determine the enthalpies of phase transitions by a non-colorimetric method.
5. The phase diagrams of carbon dioxide were examined here in some detail, but these same attributes can also be applied to the phase diagrams of other substances as well with corresponding changes in their experimental parameters.
6. Water is an exception due to its anomalous expansion, and hence the phase diagram of water is discussed to point out its departure from most other substances.
7. The vapor pressure of a liquid increases when an inert gas is added to the vapor above it, in a closed container. This is because increased pressure applied over the liquid increases its chemical potential. Since the vapor is in equilibrium with its liquid before the application of pressure, the chemical potential of the vapor also must increase to maintain the equilibrium, and this is achieved by increasing its vapor pressure.

20.10 New terms and units

Clapeyron equation, the heat of fusion, heat of solution, the heat of sublimation, molar volume change for a transition, molar entropy for a transition, phases, degrees of freedom, components, an increase of vapor pressure with pressure. No new quantities are introduced in this chapter.

$$F = C - P + 2$$

$$\ln\frac{p}{p_0} = \frac{\bar{V}_{liquid}}{R\,T}\,(\Delta p)$$

$$p = p_0\, e^{\left(\frac{\bar{V}_{liquid}}{R\,T}(\Delta p)\right)}$$

20.11 Self Reflection

1. Plot G vs U, G vs T, A vs p, and A vs q for different phases.
2. Considering your dorm space, cite examples where an increase of pressure over liquids raises vapor pressure.
3. Imagine you landed on a planet with water vapor in the atmosphere with pressure well below the triple point of water, but the temperature is about the same as on earth. Do you expect to see lakes of water, if not or if yes, why?
4. You traveled to a distant planet with an atmosphere of carbon dioxide with pressure and temperature well above the critical point of carbon dioxide. Do you expect to see liquid carbon dioxide on the surface of the planet or not, why?
5. Production of carbonated beverages uses different gas laws, mention a few of these and analyze their application to one of your favorite beverages.
6. Design an experiment for Gen Chem students to demonstrate the phase diagram of carbon dioxide.

20.12 Further Reading

1. https://ocw.mit.edu/courses/chemistry/5-60-thermodynamics-kinetics-spring-2008/video-lectures/lecture-13-gibbs-free-energy/
2. https://ocw.mit.edu/courses/chemistry/5-111-principles-of-chemical-science-fall-2008/video-lectures/lecture-18/13.6
3. https://chem.libretexts.org/Textbook_Maps/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical_and_Theoretical_Chemistry)/Thermodynamics/Energies_and_Potentials/Free_Energy/Gibbs_(Free)_Energy

20.13 Self Tests

1. The phase diagram summarizes

a. the boiling points of substances

  - b. the melting points of substances
  - c. the phase transitions of substances
  - d. chemical reactivities of substances
  - e. none of these

2. The Phase Rule connects
   - a. the degrees of freedom with the number of components and the number of phases of a system
   - b. the constituents with the number of components and the number of phases of a system
   - c. the number of phases with the number of components and the number of reactants of a system
   - d. the degrees of freedom with the number of constituents and the number of phases of a system
   - e. none of these
3. The phase diagrams describe the effect of
   - a. pressure on the phase transition temperatures of a substance
   - b. pressure on the phase boiling temperatures of a substance
   - c. temperature on the phase transition temperatures of a substance
   - d. concentration on the phase transition temperatures of a substance
   - e. none of these
4. The phase diagrams are for
   - a. only physical equilibria of pure substances
   - b. physical or chemical equilibria
   - c. chemical equilibria
   - d. solutions only
   - e. none of these
5. At the molecular level, the phase transitions indicate the strengths of
   - a. bonds
   - b. intermolecular forces
   - c. intramolecular forces
   - d. molecular force fields
   - e. none of these
6. Phase is a
   - a. physically uniform pure substance with distinct boundaries
   - b. a mixture of physically continuous and uniform pure substances with distinct boundaries
   - c. physically continuous and uniform substance with distinct boundaries
   - d. physically uniform but discontinuous substance
   - e. none of these
7. Chemical constituent is
   - a. a pure substance
   - b. an impure substance

c. a mixture of substances
d. also a chemical component
e. none of these

8. If we have a pure phase,
a. we have only one component but there can be many constituents
b. we have only one component but there can be only one degree of freedom
c. we can have only one constituent and one degree of freedom
d. we can have any number of components and constituents
e. none of these

9. At the triple point of water, the number of degrees of freedom is given as
a. one
b. zero
c. infinity
d. -1
e. none of these

10. The number of degrees of freedom of a system of 3 components and 2 phases is
a. 1
b. 2
c. 3
d. 0
e. none of these

11. At and above the supercritical point of carbon dioxide, it exists as a
a. gas
b. liquid
c. solid
d. supercritical fluid
e. none of these

12. In one of the solid, liquid, or vapor regions of the phase diagram of carbon dioxide, the number of degrees of freedom is given as
a. 1
b. 2
c. 3
d. 4
e. none of these

13. Along one of the lines bordering any two phases in the phase diagram of carbon dioxide, the number of degrees of freedom is given as
a. 1
b. 2

c. 3

d. 4

e. none of these

14. At the intersections of three lines that bordering any two phases in the phase diagram of carbon dioxide, the number of degrees of freedom is given as

a. 1

b. 2

c. 3

d. 4

e. none of these

15. The ratio of $\Delta S/\Delta V$ for the solid liquid phase transition of carbon dioxide is >0. The slope of its solid-liquid line in the phase diagram is

a. <0

b. >0

c. =0

d. infinity

e. none of these

16. The ratio of $\Delta S/\Delta V$ for the solid liquid phase transition of water is <0. The slope of its solid-liquid line in the phase diagram is

a. <0

b. >0

c. =0

d. infinity e. none of these

17. The molar volume change for solid-liquid phase transition of a substance is 5 L/mol and molar entropy change is 5 J/mol. The slope of its solid-liquid line in the phase diagram would be

a. 5 J/L

b. 1 J/L

c. (1/5) J/L

d. 0 J/mol

e. none of these

18. Application of an inert gas onto a liquid changes its vapor pressure as

a. ln (pressure applied)

b. equal to the pressure applied

c. exponential function of the pressure applied

d. a sine function of the (pressure applied)

e. none of these

19. The slope of the plot of ln (vapor pressure) vs applied pressure on a liquid is

a. <0

b. >0

c. =0

d. infinity

e. none of these

20. When an inert gas is injected into a beverage bottle with some liquid in it, the

a. flavor is diminished

b. vapor pressure of the liquid is reduced

c. vapor pressure of the liquid is increased

d. vapor pressure of the liquid is unchanged

e. none of these

20.14 Self Tests Key

1. c, 2. a, 3. a, 4. b, 5. b, 6. c, 7. e, 8. e, 9. b, 10. c, 11. d, 12. b, 13. a, 14. e, 15. b, 16. a, 17. b, 18. c, 19. b, 20. c

20.15 Problems

1. The molar volume change for solid-liquid phase transition of a substance is 5 L/mol and molar entropy change is 5 J/mol. The slope of its solid-liquid line in the phase diagram would be. (Ans. 1 J/L)
2. Explain why the solid liquid line for CO2 in the phase diagram has a negative slope while the same line in the phase diagram of water has a positive slope? What are the consequences of change in the sign of the slope for these two substances?
3. Design an experiment to measure the entropy of sublimation of solid carbon dioxide around its triple point.
4. If the rate of change of vapor pressure with respect to temperature of a liquid is 0.044 atm/K and its vapor is considered as an ideal gas, what is its molar entropy of evaporation? (Ans. 100 J/K mol)
5. If the rate change of fusion temperature of a solid is -7517 atm/K, and its molar volume change is -1.6 cc, what is its molar entropy of fusion? (Ans. 100 J/K mol).
6. An average car weighs 4000 lbs and has a tire width of 10 cm and assuming the length of the tire that comes in contact with the road is 10 cm, what is the decrease in the melting point of ice when the car drives over an ice sheet at 0 ˚C? (ΔH fusion of ice = 6.01 kJ/mol; ΔV fusion of ice = -0.00165 L/mol) (Ans. -3.3 ˚C)
7. An average coke bottle is filled with carbon dioxide to a pressure of 325 kPa. Assuming that the vapor pressure of water before filling is 1 atm, and using the molar volume of water being 18 mL/mol, what is the expected vapor pressure inside the bottle after filling with this inert gas at room temperature? Will it be safe to open a warm bottled of coke? (Ans. final vapor pressure is 1.002 atm, safe to open)
8. Design an experiment to measure the slope of the solid-liquid line for water.
9. Explain why one can skate on ice but not on concrete?
10. Explain why the 2-mile-thick glacier of the Greenland does not slip off the land, assuming it is downhill? What would be the consequence if the ground below is warmed to -5 ˚C due to global warming?

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Chapter 21. The Ideal Dilute Solution

After completing this chapter, you will be able to:

- Recognize ideal solutions, solvent, and solute.
- Apply Raoult's law solutions made of a volatile solvent and a non-volatile solute.
- Apply the concepts of chemical potential to rationalize the formation and behavior of solutions.

Goals

- Define solvent, solute, solution and an ideal solution
- State and deduce Raoult's Law and apply it binary solutions of a volatile solvent and a nonvolatile solute.
- Examine vapor pressure-composition diagrams for ideal and real solutions.
- Synthesize equations to describe the chemical potential changes of the solvent, solute and the solution, when a solution is formed.

21.1 Why study this?

We recognize that pure substances often do not exist in nature, and they need to be prepared when desired, mostly. However, there is a tendency for pure substances to form solutions spontaneously. This could be from the pure solvent and the pure solute or from other solutions as well. Nevertheless, solutions are often used for conducting or studying chemical reactions and physical processes, and solutions are everywhere around us. Thus, we ask what drives the formation of solutions from pure substances or mixtures and how is the composition of the solution controlled by thermodynamics? These questions are important to understand the molecular basis for solution formation, which is important in tailoring solutions for various practical applications. This chapter is therefore useful in understanding the behavior of solutions as most natural substances that we find in nature are indeed solutions and abundant. Solutions are often used in daily applications. For example, tea or coffee is a complex mixture containing multiple solutes such as sugar, caffeine, and other substances dissolved in it. Various flavors in these beverages that we enjoy are often present as well. Thus, the study of solutions is fascinating and important, and we begin with ideal solutions containing a nonvolatile solute, which is a simpler system to begin our studies of solutions.

21.2 Ideal Solutions

We first define some useful terms --the solvent, the solute, and the solution --then we examine what an ideal solution is. The solution is a mixture of the solvent and at least one solute that is uniformly distributed to form a single phase. Solutions can be liquids, solids, or gases, and our general perception is that they are liquids, but it is not limited to liquids. All alloys are solutions of one solid in another and considered solid solutions. The phase of the solution in these cases is solid. All gases mix spontaneously to form mixtures of gases, and that is an example of a gas-phase solution. In the case of a liquid solution, the other component can be a solid, another liquid, or a gas. Thus, a solution can be solid, liquid, or gas and should have at least a second component that is uniformly distributed in it. Thus, the solution must be at least a binary mixture of any two components forming a single phase. The solutions can be dilute, concentrated, or saturated, depending on the amount of solute dissolved in them, but the solution must be a uniform mixture or a single-phase only.

The solvent is defined as the major component of a solution, and it can be gas, liquid, or solid that is uniformly distributed in the solution. Our general perception is that a solvent is a liquid, but it need not be so. Gold is a good solvent for many metals and forms solid solutions. Pd is a good solvent for hydrogen gas and forms a solid solution as well. Water is a good solvent for many gases and hydrochloric acid, for example, is a solution of the HCl gas in water. Seawater is a solution of several salts and other materials dissolved in the solvent, water. The atmosphere contains the solvent nitrogen, which is the major component, and various other components, such as oxygen and carbon dioxide, for example, are dissolved in it. Thus, a solvent can be gas, solid, or liquid but it must be the most abundant component in the mixture and should form a uniform phase with the other components (solutes) present in it.

The solute is defined as the minor component (gas, liquid, or solid) present in a solution and distributed uniformly throughout the solution phase. The amounts of a solute are quantified in terms of their mole fractions rather than mole numbers. The solute must be completely dissolved in the solvent to be part of the solution. A saturated solution may have a solution in contact with an undissolved solute, two separate phases. Thus, only the dissolved solute is part of the solution. When the mole fraction of the solute exceeds that of the other component in a binary mixture, for example, then the solute becomes the solvent, regardless of how the solution was made initially, and the solvent becomes the solute. In fact, in all our discussions of solutions, the mole fraction of the solute approaches zero, dilute, and hence is not an issue. But, for practical considerations, the solute mole fraction does not exceed that of the solvent. For example, salt present in seawater is a solute, among others. The sugar in our tea or coffee is a solute while water is the solvent. If we examine the atmosphere's content on this planet, oxygen is a solute while nitrogen is the solvent. Thus, solutes and their solvents are abundant around us. They are also commonly used in our daily applications and encountered in commercial products as well.

The solution is defined as a homogeneous mixture of the solvent (gas, liquid, or solid) and the solute (gas, liquid or solid). It should be a single continuous phase, but it could be in equilibrium with other phases such as the solute or vapor etc., The phase containing the solution is of interest in this chapter. For example, cough syrup is a solution and the blood that is flowing in our bodies is a solution containing numerous solutes. Lakes and rivers are solutions containing dissolved matter and mineral acids are solutions of chemical substances dissolved in water. Most products that we buy are either solutions or suspensions, but suspensions are an entirely different type of system. In this chapter, we will consider only binary systems where the mole fraction of one of the solutes approaches zero or dilute solutions.

21.2.1 The concept of an ideal solution

We define the ideal solution as consisting of a solute dissolved in a solvent such that both the enthalpy of dissolution and the volume of dissolution are zero. In practical terms, real solutions approach ideal behavior when the mole fraction of the solute approaches zero, while both the enthalpy of solution as well as the volume of solution approach zero. For an ideal solution, there is no change in enthalpy or volume ($\Delta H = 0$; $\Delta V = 0$) and the implication is that we assume that there are no inter-particle interactions.

If the temperature is kept constant, then we can write $\Delta G = \Delta H - T\Delta S$ for an ideal solution ($\Delta H = 0$), and the free energy change is entirely due to the increase in the entropy of the system ($\Delta G = -T\Delta S$). We can easily argue that the entropy of the system is increasing at constant temperature because the spatial distribution of the particles is increasing as we dissolve the solute in the solvent. Thus, the solute, as well as the solvent, are more randomly distributed in the solution than in their corresponding pure phases. The formation of the ideal solution is driven solely by the increase in the entropy of the system, under isenthalpic, isobaric, isothermal, and isochoric conditions.

Example 21.1

We can fully define an ideal solution as one that satisfies the following thermodynamic criteria:

$\Delta H = 0$; $\Delta V = 0$; $\Delta G = -T\Delta S$ and since T can't be <0, ΔS must be >0. We remind ourselves that these criteria originate from the assumption that the particles of the solute and the solvent have no inter-particle interactions. This is an ideal solution, and a mixture of ideal gases is a good example. However, ideal gas does not exist, and an ideal solution does not exist. But we use these limiting models to understand the properties of real solutions at the limit of no interactions among the particles or when these interactions are negligible when compared to the thermal energies of the particles. Thus, an ideal solution results in no liberation of heat and/or change in volume when it is formed from its pure constituents and the process is spontaneously driven solely by an increase in the entropy of the system. Deviation from the ideal behavior for solutions is well known. For example, if we dissolve ammonium chloride in water, the temperature of the solution decreases rapidly -- an endothermic process. Thus, ΔH is not equal to zero and it is not an ideal solution.

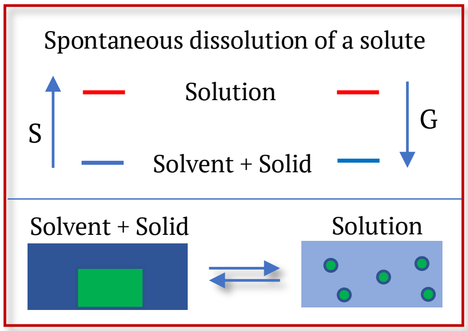

Figure 21.1 The spontaneous mixing of a solute and the solvent to form the ideal solution with an increase in the entropy of the system and a decrease in its chemical potential.

21.2.2 Volatile and nonvolatile solutes

We divide the solutes into those that are nonvolatile under ambient conditions, and volatile, those that have a measurable vapor pressure. Most solids that we encounter are not volatile and most liquids we encounter do have some vapor pressure. This difference in the volatility of the solute makes a major difference in their behavior when present in a solution, and the solution behavior is influenced by the nature of the solute. In this chapter, our discussions will be limited to nonvolatile solutes to keep things simple, and in later chapters, we will concern ourselves with volatile solutes. However, we will consider only volatile solvents in this book.

Since the solute is not volatile but the solvent is, the vapor above the solution will only contain the particles of the solvent but not the solute. For an ideal solution, we can assume that this is valid.

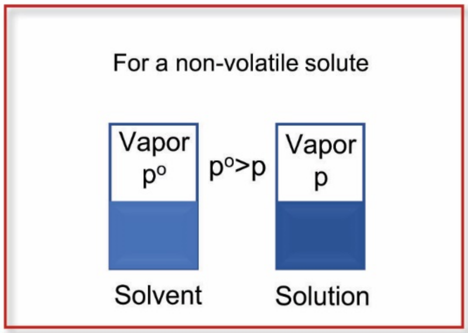

Figure 21.2 The equilibrium between the vapor of the solvent and the ideal solution consisting of dissolved nonvolatile solute. The vapor pressure of the pure solvent (left) is altered by the presence of the nonvolatile solute in the solution (right).

In Figure 21.2, the container on the left contains only pure solvent, and hence, its vapor contains only the particles of the pure solvent with a vapor pressure of p˚. One can visualize that the solvent particles at the gas-liquid interface escape into the vapor phase to occupy additional volume. Conversely, some vapor particles will return to the liquid phase and when the vapor is equilibrated with the vapor, the number of particles that leave the liquid phase and enter the vapor is exactly equal to the number of particles that leave the vapor and enter the liquid phase.

When a nonvolatile solute is dissolved in a volatile solvent to form an ideal solution (right side), the vapor above the solution still contains only the particles of the pure solvent, but the vapor pressure would have changed to p. The relation between the vapor pressure of the pure solvent (p˚) and that of the solution (p) containing a nonvolatile solute is given by Raoult's law, an ideal law of solutions.

21.3 The Raoult's law, volatile solvent, and non-volatile solute

Raoult's law states that the vapor pressure of a volatile solvent (p) in a solution containing a nonvolatile solute is proportional to the mole fraction of the solvent ($X_{solvent}$) in the solution.

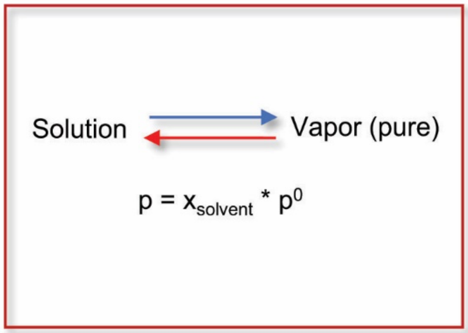

Figure 21.3 The equilibrium between the liquid solution containing a nonvolatile solute and the vapor above the solution. The vapor pressure of the solution (p) is equal to the product of the mole fraction of the solvent ($X_{solvent}$) and the vapor pressure of the pure solvent (p˚).

The law is expressed mathematically as shown in Figure 21.3 and a plot of the law is shown in Figure 21.4. The vapor pressure above the liquid must be proportional to the mole fraction of the volatile component, solvent, and the proportionality constant is obtained by imposing the limiting conditions.

$$p \propto X_{solvent}$$

When the mole fraction of the solvent approaches zero, the vapor pressure will approach zero as well because the nonvolatile solute will occupy most of the surface of the solution and has no vapor pressure.

$$p \rightarrow 0 \ when \ X_{solvent} \rightarrow 0$$

When the mole fraction of the solvent approaches 1, the vapor pressure will approach p˚ because it will essentially be the pure solvent.

$$p \rightarrow p^{\circ} \ when \ X_{solvent} \rightarrow 1$$

With these boundary conditions, we readily see that Raoult's law is as given below for an ideal solution.

$$p = p^0 \, X_{solvent}$$

When the equilibrium is reached between the vapor and the solution, the vapor pressure of the volatile solvent is linearly related to its mole fraction in the solution (Figure 21.4). The plot is linear for ideal solutions and the slope is given by the following equation:

$$p = 0 + (dp/dX_{solvent}) \, X_{solvent}$$

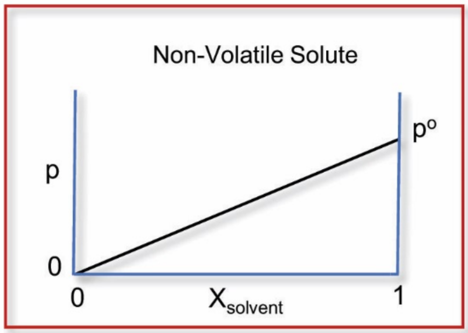

Figure 21.4 Plot of the vapor pressure of the volatile solvent of an ideal solution of the nonvolatile solute, as a function of the mole fraction of the solvent in the solution phase. The linear plot is noted only for ideal solutions or when there are no interactions between the solute and the solvent.

When the mole fraction of the solvent is 0, there is no volatile component in the system and the vapor pressure will be zero (Figure 21.4). When the mole fraction of the solvent is 1, there is no solute and hence the vapor pressure is the same as that of the pure solvent (p˚).

Example 21.2

Calculate the vapor pressure of an ideal solution consisting of a volatile solvent (water) and a non-volatile solute (NaCl) dissolved in the solvent at a concentration of 0.6 M (that of seawater). The vapor pressure of the pure solvent is 0.0313 atm.

Mole fraction of nonvolatile solute is 0.6 M salt dissolved in 55 M water, total mole numbers in 1 L is 55.6, and hence the mole fraction of the solvent is 55/55.6. The vapor pressure of water over the solution is given bin Raoult's law as:

$$p = p^0\, X_{solvent} = 0.0313\ atm * \frac{55}{55.6} = 0.309\ atm$$

Thus, the change in the vapor pressure due to salinity is negligible but on a global scale this can addup.

Analyzing this plot from the viewpoint of the mole fraction of the nonvolatile solute (Figure 21.5), we realize that when the mole fraction of the solute is zero, the vapor pressure will be due to the pure solvent (y-intercept), and when the mole fraction of the solute is 1, there will be no solute, and hence the vapor pressure drops to zero (x-intercept).

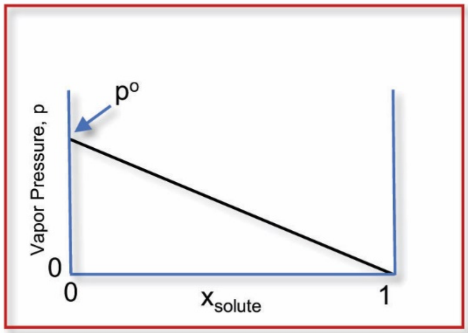

Figure 21.5 Plot of the vapor pressure of the solvent above its solution with a nonvolatile solute as a function of the mole fraction of the solute.

In summary, ideal solutions of a nonvolatile solute dissolved in a volatile solvent obey Raoult's law, and the vapor pressure is proportional to the mole fraction of the volatile solvent present in the solution phase. The highest vapor pressure is noted for the pure solvent, but the vapor pressure of the solvent varies linearly with the mole fraction of the volatile solvent present in the solution.

Example 21.3

Calculate the percent change in the vapor pressure of a solution of water and sodium chloride when the mole fraction of sodium chloride is 0.1, assuming that it is ideal.

Mole fraction of nonvolatile solute = 0.1, let p be the final vapor pressure and p˚ be the initial vapor pressure. The relative change in vapor pressure = (p-p˚/p˚)

$$p - p^{\circ} = p^0\, X_{solvent} - p^{\circ}$$

$$(p - p^{\circ}) = p^0\,(X_{solvent} - 1) = \ p^0\,(X_{ssolute})$$

$$\frac{p - p^{\circ}}{p^{\circ}} x\ 100 = (\,X_{solvent} - 1)) = (-X_{ssolute})$$

The percent change in vapor pressure is = -0.1*100% or there will be a decrease in the vapor pressure as the nonvolatile solute is added by 10%. When the mole fraction of the solute is 1, the change is -100%, which makes perfect sense.

21.4 Chemical potentials of solutions

Now, we ask why does a solution forms spontaneously from some substances while a solution is not formed for certain other substances? We expect that this has something to do with the change in the chemical potential when the solution is formed. So, we will examine the chemical potentials of the solute and the solvent in the solution and ask, what is the net change in the chemical potential when the solution is formed?

21.4.1 Chemical potential of the solvent in an ideal solution (μ1)

Consider the ideal solution consisting of a volatile solvent and a nonvolatile solute. The dissolution of the nonvolatile solute in the solution decreases the vapor pressure of the pure solvent (p˚) and to a value (p) given by Raoult's law. Let $\mu_{solvent}$ (in solution) be the chemical potential of the solvent in the solution, let $\mu^{\circ}_{solvent}$ be the chemical potential of the pure solvent (Figure 21.6, left), let μ_{solute} (in solution) be the chemical potential of the solute in the solution, and let $\mu_{solvent}$ (vapor) be the chemical potential of the solvent in the vapor phase (Figure 21.7, right).

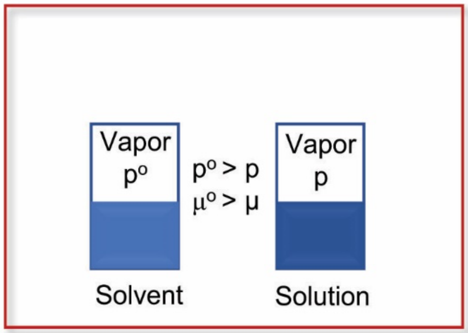

Figure 21.6 The differences in the vapor pressures of the pure solvent and its solution with a nonvolatile solute is due to the lower chemical potential of the solution, than the pure solvent or pure solute. Thus, a decrease in the chemical potential of the system drives the spontaneous formation of the ideal solution.

When the vapor above the solution reaches equilibrium (Figure 21.6, right), the chemical potential of the solvent in the solution phase should be equal to the chemical potential of the solvent in the vapor phase due to the equilibrium. We write the following equation defining this equilibrium, in thermodynamic terms.

$$\mu_{solvent}\ (in\ solution) = \mu_{solvent}\ (vapor)$$

We now write the right-side term in terms of μ°_{vapor} and its pressure, where ˚ represents 1 atm of vapor pressure (p).

$$= \mu^0_{vapor} + R\,T\ln p$$

Using Raoult's law, we write the vapor pressure of the solvent in terms of its mole fraction in the solution as follows:

$$\mu_{solvent}\ (in\ solution) = \mu^0_{vapor} + R\,T\ln p^0 + R\,T\ln X_{solvent}(in\ the\ solution)$$

Again, using Raoult's law we showed the following relation.

$$\mu^0_{vapor} + R\,T\ln p^0 = \mu^0_{solvent} \qquad \text{(Raoult's law)}$$

Substituting the above equation in the penultimate equation, we get the equation we are looking for.

$$\mu_{solvent}\ (in\ solution) = \mu^0_{solvent}\ (pure) + R\,T\ln X_{solvent}$$

We note that X <1, and ln X <0, and hence we deduce that the chemical potential of the solvent in the solution is less than that of the pure solvent.

$$\mu_{solvent}\ (in\ solution) < \mu^{\circ}{}_{solvent}$$

This decrease in the chemical potential drives the solution formation from the solvent front, and this is only part of the story, and the other part depends on the solute, which we will examine shortly.

A plot of $\mu_{solvent}$ (in solution) as a function of $X_{solvent}$, a linear plot with a negative slope and y-intercept of $\mu^{\circ}_{solvent}$ should be obtained (Figure 21.7). All ideal binary solutions containing a nonvolatile solute and a volatile solvent, obey this behavior.

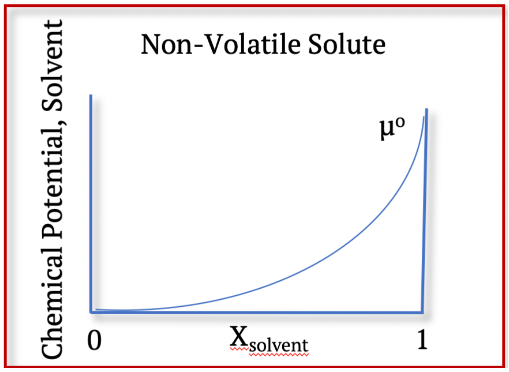

Figure 21.7 Plot of the chemical potential of the volatile solvent in the solution phase as a function of its mole fraction in an ideal solution containing a nonvolatile solute.

The ideal solution formation is driven only by the entropy increase, and hence the decrease in the chemical potential of the solute is due to entropy increase.

Example 21.4

Calculate the change in the chemical potential of water when 5 moles of sodium chloride is dissolved in 1 L of pure water (55.5 moles/L) at 300 K.

Mole fraction of solvent = moles of solvent/(moles solvent + moles of solute) = 55.5/ (55.5+5)

The relative change in the chemical potential of the solvent upon solution formation is:

$$\mu_{solvent}\ (in\ solution) - \mu^0_{solvent}\ (pure) = R\ T \ln X_{solvent}$$

Thus, the change in the chemical potential $= R\ T \ln X_{solvent} = 8.3144 \frac{J}{K\ mol} * \ln\left(\frac{55.5}{60.5}\right) = -215.2\ J/mol$

Thus, the dissolution of sodium chloride in water is a spontaneous process.

In summary, the decrease in the chemical potential of a volatile solvent during the solution formation with a nonvolatile solute contributes to the formation of the ideal solution. The maximum decrease in the chemical potential also depends on the contributions of the chemical potential of the nonvolatile solute, which we discuss next.

21.5 Chemical potential of the solute in a binary ideal solution (μ_2)

The chemical potential or the change in the chemical potential of the nonvolatile solute can be obtained similarly as above, but we can also obtain it in a simpler manner using the Gibbs-Duhem equation.

Writing the chemical potentials of the solvent (μ_1) and that of the solute (μ_2) with the subscripts of 1 and 2, for simplicity, and the corresponding mole numbers as n_1 and n_2 in an ideal mixture, we write the changes in the chemical potentials as below. We use subscript 1 for the solvent and 2 for solute for the rest of this chapter.

$$n_1\ d\mu_1 + n_2\ d\mu_2 = 0$$

Or we can argue that the changes in the two chemical potentials should be equal but opposite.

$$n_1\ d\mu_1 = -n_2\ d\mu_2$$

Rearranging and replacing the mole numbers with the corresponding mole fractions, we get the following:

$$d\mu_2 = -(n_1/n_2)\ d\mu_1 = -(X_1/X_2)\ d\mu_1$$

By differentiating $\mu_1 = \mu_1^0 + R\ T\ X_1$ with respect to X1, we get:

$$d\mu_1 = R\ T\ (1/X_1)\ dX_1$$

And substituting this in the penultimate expression, we get an expression that can be integrated readily.

$$d\mu_2 = (-\ X_1/X_2)\ R\ T\ (1/X_1)\ dX_1$$

Upon cancellation of X_1 terms, we get a better form.

$$d\mu_2 = -R\,T\,(1/X_2)\,dX_1$$

But we know that $dX_1 = -dX_2$, and thus, we get the following which can be integrated without any further manipulations.

$$d\mu_2 = R\,T\,(1/X_2)\,dX_2$$

After integration with an integration constant, we write the above as follows:

$$\mu_2 = R\,T\ln X_2 + C$$

We see that $C = \mu_2^0$ when $X_2 = 1$ and hence we write the following final expression:

$$\mu_2 = \mu_2^0 + R\,T\ln X_2$$

Thus, the chemical potential of the nonvolatile solute is less than the chemical potential of the pure solute because of $X_2<1$ and $\ln(X_2) <0$. Thus, when the solution is formed, the chemical potential of the solute decreases.

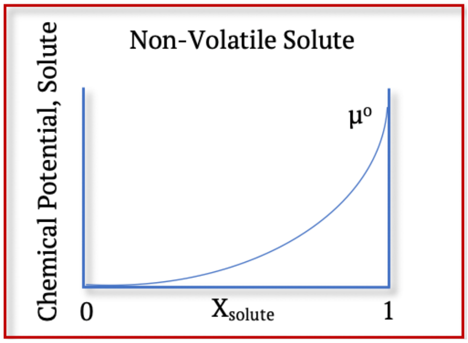

Figure 21.8 Plot of the chemical potential of the nonvolatile solute in the solution phase as a function of its mole fraction in an ideal solution containing a volatile solvent.

A plot of the chemical potential of a nonvolatile solute as a function of $\ln(x_1)$ in the solution is exponential (Figure 21.8) and the chemical potential at any stage is less than the corresponding pure component. This is the contribution of the solute for its dissolution in the solvent to form ideal solutions.

In summary, we derived an expression for the chemical potential of the nonvolatile solute in the ideal solution volatile solvent and addressed the question as to why a solute might dissolve in each solvent to form a solution. Variations on this approach are used to assess the changes in the chemical potentials of other solutions, with necessary modifications along the way.

21.6 Molecular Interpretation

The formation of a solution and the effect of a nonvolatile solute on the vapor pressure of a volatile solvent could be easily understood at the molecular level. Imagine that the beaker on the left is filled with the volatile solvent (Figure 21.9) and the gas-liquid interface at the top is occupied only with the solvent particle (open circles). Some of the solvent particles at the liquid-gas interface leave and occupy the space above the solvent creating certain vapor pressure (p˚). The pressure exerted by the vapor will be proportional to the number of molecules leaving the liquid surface as well as the number of particles re-entering the liquid phase from the vapor phase. When the particles evaporating from the surface equal to the number condensing, then we have equilibrium established.

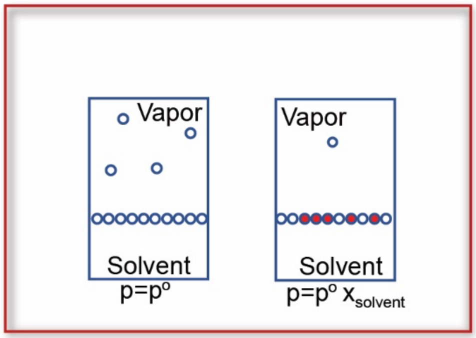

Figure 21.9 Simple explanation for the decrease in the vapor pressure of the solvent above its solution due to the presence of a nonvolatile solute.

When the solvent particles are replaced by a nonvolatile solute, there will be fewer particles that can leave the liquid surface and enter the vapor phase. Thus, the vapor pressure (p) would have decreased from the initial value of p˚. For example, a nonvolatile solute such as sodium chloride is dissolved in water and the sodium and chloride ions stay in the liquid phase water while the water molecules still can escape into the vapor phase and occupy the space above the liquid. Since the number of solvent molecules that can occupy the surface is proportional to its mole fraction, the vapor pressure of the solvent should also depend on the mole fraction of the solvent in the solution. This is Raoult's law of ideal solutions.

Gibbs free energy changes successfully predict the direction of the dissolution process, under constant temperature and pressure conditions. The chemical potential of the solution will be lower than that of the pure solvent or the solute because the particles in the solution are a mixture, have higher configurational entropy, and the dissolution is driven forward. This is true only when the solution is ideal, as considered here. Thus, the chemical potentials drive the process forward to achieve a lower potential.

21.7 Applications in daily Life

Ideal solutions do not exist, but these are model systems for dilute solutions and such dilute solutions are often encountered in our daily lives. The lotions used for eye drops, medicinal syrups, beverages, such as coffee or tea, etc., are often dilute solutions of nonvolatile solutes in water. Seawater is a dilute solution of sodium chloride in water and the presence of the non-volatile solute decreases the vapor pressure of the solvent in the atmosphere. Thus, the vapor pressure over a lake is different from that above the sea, but by a very small amount because the mole fraction of the solute in the seawater is quite small, even in the waters of the dead sea. Dilute solutions in other solvents are also encountered in various industrial applications.

21.8 Key points

1. The ideal solution is defined as the one that involves no heat of solution or change in volume. This can occur when the interparticle interactions do not exist in the solvent and the solute.
2. For an ideal solution, $\Delta S > 0$, $\Delta H = 0$, $\Delta V = 0$, and $\Delta G < 0$.
3. For an ideal solution, Raoult's law is valid at all compositions.
4. For an ideal solution formed from a volatile solvent and a nonvolatile solute, the vapor pressure of the solvent over the solution is given as the product of its mole fraction in the solution multiplied by the vapor pressure of the pure solvent.
5. The chemical potential of the solute decreases when an ideal solution is formed. Similarly, the chemical potential of a solvent decreases when an ideal solution is formed.
6. The total chemical potential of an ideal solution decreases as the solution is formed from its pure components.

21.9 New terms and Units

Raoult's law, vapor pressure, mole fraction, chemical potential, the ideal solution, ideal dilute solution. Vapor pressure, mole fraction, and chemical potential have the same units as defined earlier.

$$p = p^0\, X_{solvent}$$

$$\mu_2 = \mu_2^0 + R\,T\ln X_2$$

$$\mu_{solvent}\ (in\ solution) = \mu_{solvent}^0\ (pure) + R\,T\ln X_{solvent}$$

$$\mu_2 = \mu_2^0 + R\,T\ln X_2$$

21.10 Self Reflection

1. Plot chemical potential vs the mole fraction of a solute for an ideal solution of a nonvolatile solute and a volatile solvent.
2. In the space of your dorm room, identify examples of gas-gas, liquid-gas, liquid-liquid, liquid-solid, solid-gas, and solid-solid solutions. Discuss if any of them are nearly ideal or non-ideal solutions.
3. Based on a molecular basis, explain why a non-volatile solute decreases the vapor pressure of a volatile solvent?
4. On a molecular basis, explain why the application of an inert gas pressure induces evaporation of a solvent?
5. Deduce if the application of inert gas pressure will increase the sublimation of a solid perfume and explain your deductions on a molecular basis.
6. When a supersaturated salt solution is disturbed, you will get sudden crystallization of salt while the solution even warms up rapidly. Explain this process using chemical potential-mole fraction diagrams.

21.11 Further Reading

1. https://ocw.mit.edu/courses/chemistry/5-60-thermodynamics-kinetics-spring-2008/video-lectures/lecture-21-ideal-solutions/2.https://ocw.mit.edu/courses/chemistry/5-111-principles-of-chemical-science-fall-2008/video-lectures/lecture-18/13.6
2. https://ocw.mit.edu/courses/chemistry/5-60-thermodynamics-kinetics-spring-2008/video-lectures/lecture-20-phase-equilibria-2014-two-components/

21.12 Self Tests

1. The key assumption made in describing ideal solutions is

   a. enthalpy change is zero

   b. volume change is zero

   c. entropy change is zero

   d. Gibbs free energy change is zero

   e. both a and b

2. The key assumption made in describing the ideal solution is

   a. the interparticle interactions in the solution are very large

   b. the interparticle interactions in the solution are negligible

   c. the interparticle interactions in the solution are attractive

   d. the interparticle interactions in the solution are repulsive

   e. none of these

3. The experimental test for the formation of an ideal solution is

   a. that $\Delta G > 0$

   b. that $\Delta H > 0$

   c. that $\Delta V > 0$

   d. Raoult's law is obeyed over all compositions

   e. none of these

4. The chemical potential of solution
    - a. decreases when an ideal solution is formed
    - b. increases when an ideal solution is formed
    - c. is unchanged when an ideal solution is formed
    - d. can't say
    - e. none of these
5. When an ideal solution is formed, the chemical potentials of the solute and solvent
    - a. increase
    - b. decrease
    - c. do not change
    - d. one increases while the other decreases accordingly
    - e. none of these
6. The effect of a nonvolatile component on the vapor pressure of a volatile solvent in an ideal solution is
    - a. increase the boiling
    - b. decrease the vapor pressure
    - c. none
    - d. both a and b
    - e. none of these
7. A solvent can be
    - a. only a liquid
    - b. a liquid or a solid
    - c. a liquid, solid or a gas
    - d. both a and c
    - e. none of these
8. When a solution is formed spontaneously, ideal, or not, the following decreases.
    - a. chemical potential of the system
    - b. enthalpy of the system
    - c. entropy of the system and the surroundings
    - d. both a and c
    - e. all of the above
9. Slope of the plot of vapor pressure on the y-axis and mole fraction of the solvent on the x-axis for an ideal solution of a nonvolatile solute and volatile solvent is
    - a. >0
    - b. <0
    - c. $=0$
    - d. can't say
    - e. none of these

10. Slope of the plot of vapor pressure on the y-axis and mole fraction of the solute on the x-axis for an ideal solution of a nonvolatile solute and volatile solvent is

a. =0

b. <0

c. >0

d. molar entropy

e. none of these

11. Plot of the chemical potential of a volatile solvent as a function of its mole fraction, present in an ideal solution of a nonvolatile solute, has y-intercept equal to

a. the boiling point

b. freezing point

c. sublimation point

d. infinity

e. none of these

12. The chemical potential of the solute (μ_2) in an ideal solution is related to its chemical potential in the pure form (μ°_2) mole fraction (X_2) as

a. $\mu_1 = \mu_2^0 + R\,T\ln X_2$

b. $\mu_2 = \mu_2^0 + R\,T\ln X_1$

c. $\mu_2 = \mu_2^0 - R\,T\ln X_2$

d. $\mu_2 = \mu_2^0 + R\,T/\ln X_2$

e. none of these

13. The chemical potential of the solvent (μ_1) in and ideal solution is related to its chemical potential in the pure form (μ°_1) mole fraction (X_1) as

a. $\mu_1 = \mu_2^0 + R\,T\ln X_2$

b. $\mu_2 = \mu_1^0 + R\,T\ln X_1$

c. $\mu_2 = \mu_2^0 - R\,T\ln X_1$

d. $\mu_1 = \mu_1^0 + R\,T\ln X_1$

e. none of these

14. The Raoult's law of solutions is

a. $p = p^0\,X_{solvent}$

b. $p = p^0\,X_{solute}$

c. $p = p^2\,X_{solvent}$

d. $p = p^1\,X_{solvent}$

e. none of these

15. For an ideal solution of a volatile solvent and a nonvolatile solute,

a. $p\ \to 0\ when\ X_{solvent} \to 1$

b. $p\ \to 0\ when\ X_{solvent} \to 0$

c. $p \rightarrow 1 \; when \; X_{solvent} \rightarrow 0$

d. both a and c

e. none of these

16. The relative change in the vapor pressure of water when the mole fraction of sodium chloride of 0.1 is dissolved in it to form an ideal solution is

a. -10%

b. 10%

c. -0.1%

d. -1%

e. none of these

17. The relative change in the vapor pressure of water having a mole fraction of sodium chloride of 1 would be

a. -10%

b. 100%

c. -0.1%

d. -10%

e. none of these

18. The change in the chemical potential of a volatile solvent (50 moles) when 5 moles of a nonvolatile solute is dissolved in it, at 300 K, is

a. -227.74 J/mol

b. 237.74 J/mol

c. -237.74 J/mol

d. can't say

e. -237.74 kJ/mol

19. When a solute dissolves spontaneously in a solvent to form an ideal solution, the chemical potential of the entire system

a. increases

b. does not change

c. is at equilibrium

d. decreases

e. can't say

20. When a supersaturated solution produces a crystalline solute, the chemical potential of the system

a. increases

b. decreases

c. can't say

d. does not change

e. none of the above

21.13 Self Tests Key

1. e, 2. b, 3. d, 4. a, 5. b, 6. d, 7. c, 8. a, 9. a, 10. b, 11. e, 12. e, 13. d, 14. a, 15. b, 16. a, 17. e, 18. c, 19. d, 20. b

21.14 Problems

1. What is the relative change in the vapor pressure of water when the mole fraction of sodium chloride of 0.1 is dissolved in it to form an ideal solution? (Ans. -10%)
2. One estimate is that 750 billion tons of ice is melting each year due to global warming. Assuming that all ice is of fresh water, what is the increase in the vapor pressure of oceans due to this additional melting ice? Currently, 0.6 M NaCl is present in 321,000,000 cubic miles of seawater, and assume that decrease in vapor pressure of seawater is due to this one non-volatile solute and that density of all water is constant at a uniform temperature of 25 ˚C. (Ans. ~0.1 %)
3. A can of a popular beverage is estimated to have 50 g sugar for 500 mL. What is the decrease in the water vapor pressure due to the addition of this nonvolatile solute, assume ideal behavior? (Ans. -0.00018 atm)
4. The dead sea has one of the highest concentrations of dissolved salts, with a salinity of 342 g/kg. What is the difference in the chemical potential of this seawater from that of pure water, if all its salinity is due to NaCl. (Ans. -373.00 J/mol)
5. What is the relative change in the vapor pressure of water having a mole fraction of sodium chloride of 1 in it would be? (Ans. -100%)
6. What is the change in the chemical potential of a volatile solvent (50 moles) when 5 moles of a nonvolatile solute are dissolved in it, at 300 K? (Ans. -237.74 J/mol)
7. Design an experiment to demonstrate the reduction in the vapor pressure of water when 10 moles of sodium chloride dissolves in it over a period of 10 minutes, gradually, at 25 ˚C.
8. In a small, closed container, 1 M NaCl solution and pure water are kept separately in open containers inside this closed container. What would you expect to happen over time if nothing is disturbed?

Chapter 22. Colligative Properties and NanoChemistry

After completing this chapter, you will be able to:

- Recognize the colligative properties of dilute solutions of non-volatile solutes and suspensions of nanoparticles.
- Relate the decrease in vapor pressure, increase of boiling point, or a decrease of freezing point with the changes in the chemical potentials of the corresponding phases.
- Apply these concepts to measure molecular mass and particle mass in advanced nanotechnology.

Goals

- Synthesize equations connecting the changes in the chemical potentials of solution, solvent, solute with mole fractions.
- Predict the changes in the melting point, boiling point and the sublimation points of solutions containing a nonvolatile solute and a liquid solvent.
- Investigate the phenomenon of the osmotic pressure and synthesize the van ‘t Hoff equation connecting the molar mass of the solute with the osmotic pressure.
- Apply these concepts to suspensions of nanoparticles

22.1 Why study this?

In the previous chapter, we recognized that the dissolution of a nonvolatile solute dissolved in a volatile solvent lowers the chemical potential of the solvent. One consequence we discovered was that the vapor pressure of the solvent decreased to match the chemical potentials between the two phases that are in equilibrium. We now predict that one consequence of the decreased vapor pressure of the vapor above the solution is that the boiling point of the solution must increase. This is because the vapor pressure is lowered by the solute, and we need to heat the solution to a higher temperature to equal the vapor pressure to that of the atmosphere. The presence of a nonvolatile solute is, thus, anticipated to elevate the boiling point of the solution containing the nonvolatile solute.

Going one step further along these arguments, we predict that the freezing point of the solution should decrease as well. At the freezing point, the chemical potential of the solid equals that of the liquid, but the chemical potential of the solution is lowered by the solute and hence the chemical potential of the solution equals that of the pure solid at a lower temperature than normal (chemical potential decreases with temperature). Thus, the solution should freeze at a lower temperature than the pure solvent itself.

In another vein of arguments presented above, we predict that the pure solvent should spontaneously mix with the solution to decrease its chemical potential because the solution has a lower chemical potential than the pure solvent. This seems trivial but when the solvent and solution are separated by a semi-permeable membrane, this leads to the phenomenon of osmosis. When the solution and the solvent are in equilibrium across a semipermeable membrane, their chemical potentials must be equal. But they are not initially when brought in contact. The situation is remedied when the solvent rushes across the membrane and mixes with the solution raising its hydrostatic column, thus increasing the pressure over the solution. Thus, the solution will be at a higher pressure than the atmospheric pressure or the pressure over the pure solvent, so that the chemical potentials across the membrane are equalized. This leads to the phenomenon of osmosis which is of immediate significance in the purification of seawater via reverse osmosis.

Thus, we ask, how do these processes work, and how do we control the outcomes in a predictable, thermodynamic manner? In the end, we recognize that the above three properties, the elevation of the boiling point, lowering of the freezing point, and the osmotic pressure, depend on the concentration of the solute. These are called the colligative properties.

The properties also depend on the molar mass of the solute particles, and the above methods served to measure the molecular masses in the last century. These same classical methods are now being re-discovered to study nanoparticles and nanosystems to measure their molecular masses and examine the properties of their solutions in biological fluids, such as water.

Thus, the colligative properties are finding modern applications. These are also fully relevant to our industrial needs, and they are often encountered in our daily lives, as enumerated below.

22.2 Phase Transitions and Colligative Properties

We will consider a two-component, binary solution consisting of a nonvolatile solute and a volatile solvent, as in the previous chapter, and examine the effect of the solute on the boiling point and melting point of the solution. Later, we will consider osmosis as well.

One assumption made here is that the solute does not dissolve in the solid solvent. This is often the case in most binary systems that we are interested in. We also remind ourselves that the solute is also not present in the vapor phase because it is nonvolatile. Thus, in a phase diagram, only the liquid phase has the solute but not the other phases.

Consider the plot of the chemical potential vs the temperature of the pure solvent (Figure 22.1), which we discussed earlier (blue lines). The solid, liquid and vapor lines intersect at the corresponding melting point (Tm) and boiling point (Tb), as pointed out by the perpendiculars dropped from these intersections.

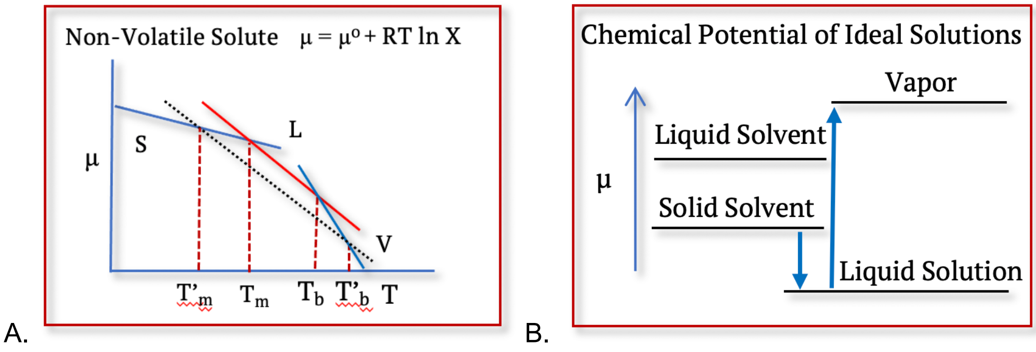
Non-Volatile Solute $\mu = \mu^o + RT \ln X$
μ
S
L
V
T'_m
T_m
T_b
T'_b
T
A.
Chemical Potential of Ideal Solutions
Vapor
Liquid Solvent
μ
Solid Solvent
Liquid Solution
B.

Figure 22.1A Plot of chemical potentials of the solid, liquid, and vapor phases of the pure solvent intersect at the corresponding boiling point (T_b) and the melting point (T_m). The black dotted line shows the chemical potential of the ideal solution of a nonvolatile solute as a function of temperature. The lowering of the chemical potential of the solution elevates the boiling point (T'_b) and the lowering of the melting point (T'_m). B. The chemical potentials of pure solid solvent, pure liquid solvent, and pure vapor phase are unaffected by the nonvolatile solute while that of the liquid solution is less than that of all three phases.

Using the notation introduced in the previous chapter that solvent is represented as component 1 and the solute as the component 2, we write the chemical potential of the solvent (μ_1) in the solution in terms of the chemical potential of its pure phase (μ°_1), its mole fraction (x_1) and temperature (T).

$$\mu_1 = \mu_1^0 + R\,T\,X_1$$

Thus, as the solute is dissolved in the solvent, the solvent mole fraction is less than 1 and the second term on the right is negative or <0. The chemical potential of the solution containing the nonvolatile solute (black dotted line) must be below the corresponding red line for the pure solvent. This expectation is justified by the above relation where the chemical potential of the solvent containing the solute is less than that of the pure solvent (Figure 22.1B). Consequently, the dotted line intersects that of the pure vapor line (blue line) at a higher temperature T'_b. Thus, the solution needs to be heated to a higher temperature for its chemical potential to be equal to that of the pure vapor. So, the boiling point of the solution is elevated over that of the pure solvent.

Another consequence of dropping the liquid line (dotted black line) is that it intersects the blue line of the pure solid at a lower temperature (T'_m) than the melting point of the pure solid (T_m). Thus, the freezing point of the solution is lowered. Then, the chemical potential diagram clearly explains the reason for the elevation of the boiling point and the lowering of the freezing point.

Now, we examine the phase diagram of the solution, where the pure liquid phase is replaced by the binary solution containing the nonvolatile solute. The solute is present only in the liquid phase but not in the solid or the vapor phases. The solid phase separates in its pure form when the solution is frozen, and when the solution evaporates or boils, the solute is left behind in the liquid phase because the solute is not volatile.

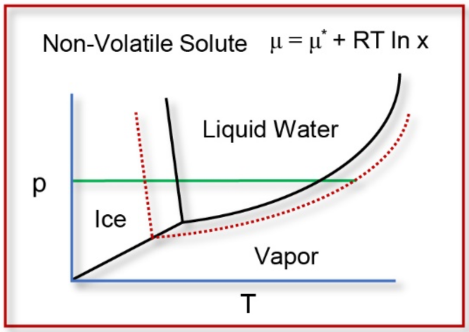

Figure 22.2 The changes in the phase diagram of a pure solvent when a nonvolatile solute is dissolved to form an ideal solution.

In the phase diagram (Figure 22.2), the red lines represent the phase transitions of the pure solvent and its solid, liquid, and vapor regions that are in equilibrium at specified pressure and temperature. When we dissolve the nonvolatile solute in the solvent and make the solution, we decrease the chemical potential of the solution and lower its vapor pressure. Thus, the boiling point of the solution is elevated at every point along the liquid-vapor line (green horizontal line). Consequently, the red dotted line, corresponding to the solution, is dropped below that of the pure solvent line.

Similarly, the solution freezes at a lower temperature than the solvent, and hence the solid-liquid line shifts to the left, but the effect on the freezing point is opposite to that of the boiling point. That is, the freezing point of the solution is lower than the pure solvent and stays to the left of that of the pure solvent. The red dotted line of the solid-liquid equilibrium of the solution is to the left of that of the pure solvent.

In summary, the decrease in the chemical potential of the solvent present in a binary solution is responsible for the decrease in its vapor pressure, the elevation of the boiling point, as well as the lowering of the freezing point. In the following sections, we examine these effects more quantitatively and relate the boiling point and the freezing point changes to the mole fractions of the solute in the solution.

22.3 Elevation of the Boiling Point

Heating a kettle of water on the stove raises its temperature until it commences to a boil (Figure 22.3). At the boiling point, we achieve equilibration between the liquid and the vapor, and their chemical potentials are equal. When a small amount of a nonvolatile solute, such as sodium chloride, is added to it, the saltwater requires a higher temperature to boil. We ask the question, what is the quantitative relation between the mole fraction of the nonvolatile solid and the elevation of the boiling point of the solution?

Figure 22.3 A kettle of water boiling on a stove, whose boiling point may be elevated by the addition of a pinch of salt, thus facilitating faster cooking (Wikipedia).

We write the liquid-vapor equilibrium and write the chemical potential of the solution to be equal to that of the pure vapor in equilibrium with it.

$$\text{Liquid} \overset{\text{Tb}}{\rightleftharpoons} \text{Vapor}$$

$$\mu^0_{vapor} = \mu_{solution}$$

The chemical potential of the solution (μ1) is written in terms of that of the pure solvent (μ˚1) and the mole fraction of the solvent (x1).

$$\mu^0_{vapor} = \mu_{solution} = \mu^0_{solvent} + R\,T \ln x_1$$

We rearrange this equation and write RT ln X1 in terms of the difference in the chemical potentials, as follows:

$$R\,T\,ln\,x_1 = \mu^0_{vapor} - \mu^0_{solvent}$$

$$ln\,x_1 = \left(\mu^0_{vapor} - \mu^0_{solvent}\right)/R\,T$$

The difference between the chemical potentials of the pure vapor and the solvent is the molar free energy (ΔG_{vap}) of evaporation.

$$\ln x_1 = \Delta G_{vapor}/R\,T$$

We can write this, in terms of the corresponding enthalpy and entropy terms, as below and then separate out the entropy term.

$$\ln x_1 = \left(\Delta H_{vapor} - T\,\Delta S\right)/R\,T$$

$$\ln x_1 = \left(\Delta H_{vapor}/R\,T\right) - \Delta S/R$$

Differentiating the above with respect to temperature, and then integrating the resulting differential equation with the limits of 1 to x_1 (pure solvent) corresponding to the boiling point of T_o and T, we get the desired expression.

$$\ln x_1 = \Delta H_{vapor}\ (1/R)\ (1/T - 1/\,T_0)$$

$$\ln x_1 = [\Delta H_{vapor}/R]\ \ (1/T - 1/\,T_0)$$

A plot of ln x_1 vs 1/T, where T is the boiling point of the solution, gives a linear plot with a slope of $\Delta H_{vapor}/R$ (Figure 22.4).

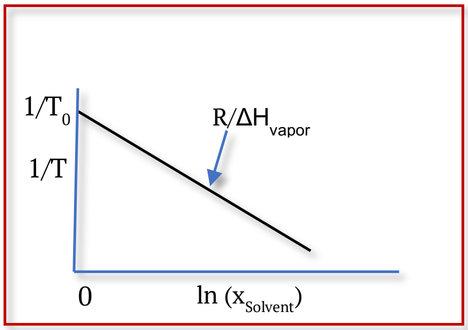

Figure 22.4 Plot of the inverse of the boiling point of an ideal solution of a nonvolatile solute as a function of the mole fraction of the solvent. The slope of the linear plot is positive and equals $\Delta H_{vapor}/R$.

At this stage, we introduce the change in the boiling point (ΔT = (T-To)) and the mole fraction of the solute (x_2) into the above equation. Making the substitution ln(1-x_2) = ln (x_1), use the common denominator to get the following:

$$ln\,x_1 = ln(1 - x_2) = [(T_0 - T)/TT_0]\ \left(\Delta H_{vapor}/R\right)$$

We approximate that for small values of x_2, ln(1-x_2) = -x_2, and write the simpler expression.

$$-x_2 = [(-\Delta T)/TT_0]\ \left(\Delta H_{vapor}/R\right)$$

We cancel the negative signs and examine ΔT vs x_2 as follows:

$$[(\Delta T)/T] = (x_2)(RT_0/\Delta H_{vapor})$$

The value of ΔT/T increases as the mole fraction of the solute increases. As x_2 approaches zero, ΔT/T approaches 0, as one would have anticipated from the boundary condition. A plot of ΔT/T as a function of x_2 gives a line with a slope equal to ($RT_0/\Delta H_{vapor}$) (Figure 22.5).

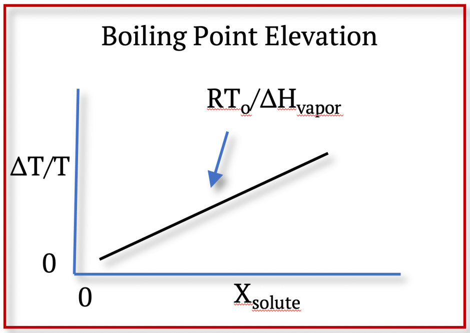

Figure 22.5 Plot of ΔT/T as a function of mole fraction of the solute, for an ideal solution of a nonvolatile solute, gives a linear plot with a positive slope equal to $RT_0/\Delta H_{vapor}$.

Since x_2 is small, we can also write it as equal to $\ln(x_2)$ and get the following classic expression.

$$-\ln X_2 = \left(\frac{\Delta H_{vapor}\,\Delta T}{R\,T\,T_0}\right)$$

From the value of the ΔT/T, we obtain the value of x_2, and from this, we deduce the molar mass of the solute by simple algebraic manipulations. We know the weight of the solvent and the solute, and if we know the molar mass of the solvent, we can calculate the molar mass of the solute.

In the early part of the 19th and 20th centuries, the elevation of the boiling point was used to determine the molecular weights of substances, and this was later replaced by modern mass spectrometry. However, in the 21st century, this method is now being rediscovered to determine the molecular masses of nanoparticles or nanomaterials that are not amenable for mass spectrometric analysis.

Example 22.1

Calculate the elevation of the boiling point of water containing 0.1 mol of sodium chloride in 1 mol of water.

Mole fraction of water =x_1 = 1/1.1; Normal boiling point of water = (T_1) = 373.1 K; ΔH_{vapor} = 40.66 kJ/mol; R = 8.3144 J/K mol

$$\ln x_1 = [(T_0 - T)/TT_0](\Delta H_{vap}/R)\ \ or$$

$$T_2 = \frac{T_1 \frac{\Delta H}{R}}{(T_1 \ln(x_1) + \frac{\Delta H}{R})} = \left(\frac{373.15\ K\ \frac{40660\ J/mol}{8.3144\ J/mol\ K}}{(373.15\ K * \ln(1/1.1) + \frac{40660\ J/mol}{8.3144\ J/mol\ K})}\right) = 375.88\ K$$

Substituting the values from above into the above equation, ΔT = 2.734 K

In summary, we answered the question, what is the effect of a nonvolatile solute on the boiling point of a solution, and we quantified the change in the boiling point of the solution with the molar mass of the solute. By knowing the molar mass of the solvent, the weights of the solvent, and the solute, the molar mass of the solute can be calculated from the boiling point data. Next, we use a similar approach to examine how the presence of the nonvolatile solute would change the freezing point of the solution.

22.4 Lowering of the Freezing Point

As the solution is cooled to freeze, only the pure solvent freezes to the pure solid, leaving all the solute in the solution. We notice that the solution freezes at a lower temperature than the pure solvent. Seawater, for example, freezes at a lower temperature than river water or that of a freshwater lake. Thus, this observation of the lowering of the freezing point is analyzed quantitatively. Consider the solution-solid equilibrium (Figure 22.6) and the chemical potentials of the two phases are equal.

$$\mu^0(solid) = \mu(solution)$$

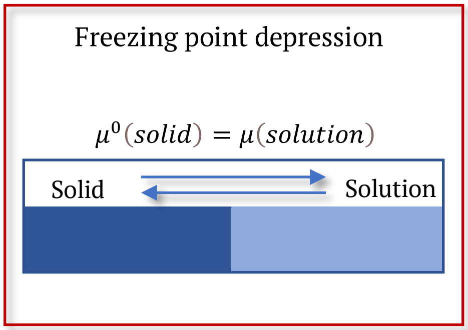

Figure 22.6 The solid-liquid equilibrium, where pure solid (left) is in equilibrium with the liquid solution (right). The chemical potentials of the two phases are equal when the equilibrium is achieved.

We write the chemical potential of the solution in terms of the pure solvent and its mole fraction in the solution as follows:

$$\mu^0(solid) = \mu(solution) = \mu^0(solvent) + R\,T\ln x_1$$

As before, the difference in the chemical potentials of the pure solid and the pure solvent is the Gibbs free energy of freezing (-ΔG$_{fusion}$), and we replace the ΔG term with the corresponding ΔH and ΔS terms.

$$\mu^0(solid) - \mu^0(solvent) = -\Delta G_{fusion} = R\,T\ln x_1$$

So, the mole fraction of the solvent is related to the enthalpies and entropies of fusion as follows:

$$ln\,x_1 = \left(-\,\Delta H_{fusion}/R\,T\right) + \Delta S_{fusion}/R$$

We differentiate the above equation with respect to temperature, assuming that both the enthalpy and the entropy terms are independent of temperature over the narrow range we encounter, we get the following differential equation:

$$(1/x_1)\,dx_1 = -\left(\Delta H_{fusion}/R\,T^2\right)dT$$

Integration with the limits of one and x1 on the left corresponding to To and T on the right side, we get the following equation:

$$ln\,x_1 - ln\,1 = \left(-\,\Delta H_{fusion}/R\right)(1/T - 1/T_0)$$

Rearrangement of the above equation readily gives the relation we are looking for, where the mole fraction of the solvent and the freezing point are inversely related.

$$\frac{R\,ln\,x_1}{\Delta H_{fusion}} = \frac{1}{T} - \frac{1}{T_0}$$

Then, a plot of 1/T vs ln(x_1) should give a straight line with a slope equal to –R/ΔH$_{fusion}$, as indicated below.

$$\frac{1}{T} = \frac{1}{T_0} + \frac{R\,ln\,x_1}{\Delta H_{fusion}}$$

We recognize that ΔH$_{fusion}$ is generally positive for most liquids, and the above plot should give a positive slope (Figure 22.7).

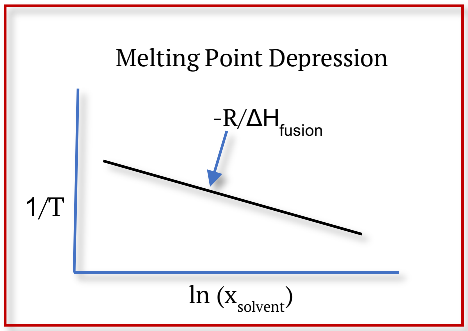

Figure 22.7 Plot of the inverse of the freezing point as a function of the ln of the mole fraction of the solvent in a solution containing a nonvolatile solute is linear with a slope equal to ($R/\Delta H_{fusion}$).

Therefore, by measuring the freezing points of a few solutions as a function of the mole fraction of the solvent containing the nonvolatile solute, the molar mass of the solute is estimated.

Example 22.2

Calculate the freezing point of a solution containing 0.1 mole fraction of a dissolved nonvolatile solute in a solvent of enthalpy of fusion of 8303 J/mol at 300 K.
ΔH_{fusion} = 8303 J/mol; R = 8.3144 J/K mol

$$\frac{1}{T} = \frac{1}{T_0} - \frac{R \ln x_1}{\Delta H_{fusion}} = \frac{1}{300\ K} - \frac{8.3144 \frac{J}{K\ mol} \ln(0.9)}{8303 \frac{J}{mol}} = 0.000333\ or\ T = 290.79\ K$$

In summary, the dissolution of a nonvolatile solute in a solvent decreases the freezing point and the decrease is quantitatively related to the mole fraction of the solvent in the solute. The nonvolatile component lowers the freezing point of the binary solution The decrease in the freezing point depends on the number of particles in the solution. Hence, this is another method to determine the molar masses of the nanoparticles because temperature can be measure with higher and higher accuracies. Next, we examine the phenomenon of osmosis.

22.5 The Osmosis

When a solution is brought in contact with the corresponding pure solvent via a semipermeable membrane, the solvent diffuses freely into the solution until the chemical potential of the solution equals that of the solution. The pressure on the solution side of the membrane increases due to the diffusion of the solvent (Figure 22.8A) and the chemical potential increases with pressure. Thus, the solvent at pressure (p) and the solution at a higher pressure (p+π) are at equilibrium, and their chemical potentials are equal. The excess pressure π is the osmotic pressure and it is related to the mole fraction of the solute. There is a detailed explanation for this observation and the ensuing derivation that led to winning the first Nobel Prize in Chemistry by Victor Van 't Hoff in 1901.

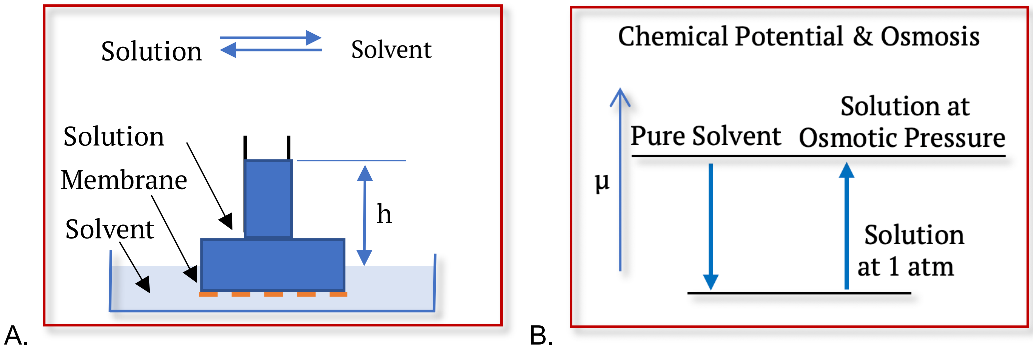

Figure 22.8 The apparatus used to measure the osmotic pressure of a nonvolatile solute dissolved in a solvent with a semipermeable membrane separating the pure solvent (bottom) and the solution (top). The height 'h' is the hydrostatic column exerting the osmotic pressure π. B. The chemical potential of the solution is lowered by the dissolution of the solute, and it equals that of the pure solvent only under the osmotic pressure applied over the solution. A pressure equivalent to osmotic pressure or more is required to produce pure solvent from the solution by reverse osmosis.

The osmotic pressure π is measured by the hydrostatic pressure due to the column of height h, and the chemical potential of the solution equals that of the pure solvent only when a pressure equivalent to the osmotic pressure is applied over the solution (Figure 22.8B). This is how pure solvent can be produced by reverse osmosis. We ask, how is the osmotic pressure related to the mole fraction of the solute? The van 't Hoff equation, derived below, explains the relation between the osmotic pressure and the mole fraction of the solute.

22.6 The Van 't Hoff Equation

When the equilibrium between the solvent and the solution across the membrane has been established, the chemical potential of the pure solvent under pressure p and temperature T, ($\mu^0_{1,(T,p)}$), is equal to the chemical potential of the solution under the pressure p+π and temperature T, ($\mu_{solution\,(T,p+\pi)}$), where π is the pressure due to the hydrostatic column above the solution. This condition is expressed mathematically as follows:

$$\mu^0_{1,(T,p)} = \mu_{solution,(T,p+\pi)}$$

We write the right-side term, the chemical potential of the solution, in terms of the chemical potential of the pure solvent at pressure p+π and its mole fraction (x_1).

$$\mu^0_{1,(T,p)} == \mu^0_1\,(T,p+\pi) + R\,T\ln x_1$$

As before, we rearrange the equation and look at this in a slightly different form.

$$-R\,T\ln x_1 = \mu^0_1\,(T,p+\pi) - \mu^0_1\,(T,p)$$

The right side of the above equation can be obtained by integrating the fundamental relation, dμ = (V/n)dp with appropriate limits, as shown below.

$$\int_{\mu(p)}^{\mu(p+\pi)} d\mu = \int_p^{p+\pi} \bar{V}\,dp$$

Upon integration, we get the right-side in terms of the molar volume of the solvent and the osmotic pressure as follows:

$$\mu^o\,(T,p+\pi) - \mu^o\,(T,p) = \bar{V}\,(p+\pi-p)$$

Substituting the above in the penultimate equation, we get the relation between the mole fraction of the solvent and the osmotic pressure where n_1 is the number of moles of the solvent.

$$-\,R\,T\ln x_1 = V\,\pi/n_1$$

We substitute $x_1 = 1\text{-}x_2$ and expand the ln function around small values of x_2, as equal to – x_2.

$$R\,T\ln(1-x_2) = R\,T\,x_2 = V\,\pi/n_1$$

We recognize that $X_2 = n_2/(n_1+n_2)$, and since the mole numbers of the solute are very small when compared to the mole number of the solute, we write n_1+n_2 as equal to n_1, and then $x_2 = n_2/n_1$. Substituting this value for x2, we get the final expression for the osmotic pressure in terms of the mole numbers of the solute and the volume of the pure solvent present in the solution.

$$R\,T\,n_2 = V\,\pi$$

The above looks exactly like the ideal gas law where the pressure is replaced by the osmotic pressure, the mole numbers are those of the solute, and the volume is that of the solvent in the solution.

$$\pi = n_2\,R\,T/V$$

The volume is written in terms of the concentration of the solute in the solvent present in the solution as follows:

$$\pi = C\,R\,T$$

This is the famous van 't Hoff equation that resulted in the Nobel prize in 1901.

Example 22.3

Calculate the osmotic pressure when 1 mole of nonvolatile solute was dissolved in 1 L of the solvent at room temperature.

$$\pi = n_2\,RT/V = 1\,mol * 0.082\,L\frac{atm}{K\,mol} * 278.15\,K * \frac{1}{1L} = 24.47\,atm$$

Substituting the above in the equation for the osmotic pressure, $\pi = 24.47$ atm.

One step further, the concentration is expressed in terms of the mass of the solute (w_2) and its molar mass (M_2), as C = (w_2/M_2V). Thus, we conclude that the osmotic pressure is inversely related to the molar mass of the nonvolatile solute.

$$\pi = w_2\,R\,T/M_2\,V$$

Thus, the smaller the molecular weight of the solute, the greater would be the osmotic pressure, independent of the molar mass of the solvent. So, there will be a big difference between sodium chloride and potassium chloride or sodium chloride versus magnesium chloride. These differences in the osmotic pressures make significant differences in biological systems and influence their biochemistry. This is one of the reasons why salt water is not good for drinking and most cells cannot survive high concentrations of these electrolytes.

Example 22.4

Calculate the molar mass of a solute of 3.05% by weight solution in water that exerts an osmotic pressure of 10 atm at room temperature?

$$\pi = W_2\,RT/M_2V \;\; or \;\; M_2 = W_2\,RT/\pi V = 30.5\,g * 0.082\,L\frac{atm}{K\,mol} * 278.15\,K * \frac{1}{10\,atm\,1L} = 74.6\,g/mol$$

In summary, we investigated the phenomenon of osmotic pressure and through the use of the chemical potential, we obtained a relation between the osmotic pressure and the molar mass of the solute. The osmotic pressure is inversely proportional to the molar mass of the nonvolatile solute and depends on the number of particles in solution. The direct proportion of the osmotic pressure with the number of moles of the particles in the solution, by far this is one of the most sensitive colligative properties for estimating nanoparticle molar masses. Pressure is also one of the most easily measurable parameters making this colligative property one of the most promising for nanoscience.

22.7 Entropy effects

In addition to the intermolecular forces (enthalpy effects) there are other factors that control the colligative properties of substances. One such is entropy (Figure 22.9A). Even though the solvent particles have sufficient energy to break away from the solvent and result in boiling, the liquid containing a nonvolatile solute does not boil until the temperature increases greater than its normal boiling point. This requirement is isentropic. Since the solution has higher entropy than the pure solvent, dispersion of the liquid into the vapor phase requires a smaller increment in entropy (Figure 22.9). Since ∆H does not change when the ideal solution is made (Figure 22.9A), enthalpic gap remains the same but the smaller entropy gap requires a higher temperature for the liquid to vapor phase transition. Thus, thermodynamic and molecular interpretations are intertwined here.

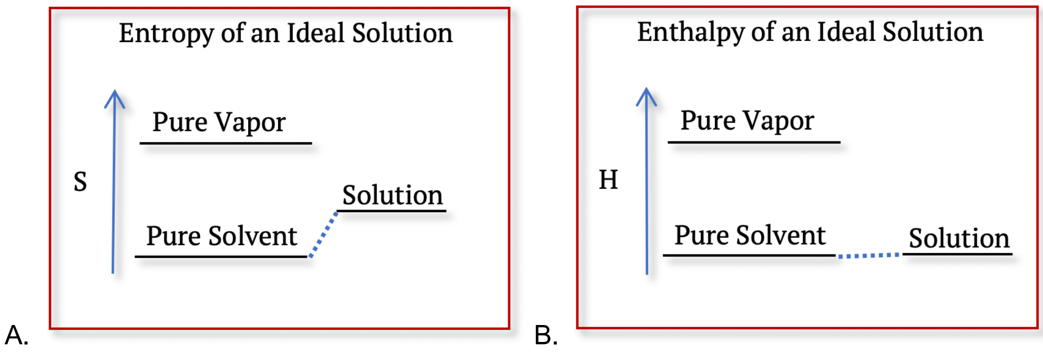

Figure 22.9 The entropies and the enthalpies of the pure solvent in the liquid state, the solution state, and the vapor state. A smaller entropy gap between the vapor and the solution suggests less facile vapor formation and elevation of the boiling point since the $\Delta H_{solution}$ is zero.

A similar explanation can be put forth for the lowering of the freezing point, but the only difference is that the pure solid has lower entropy than the solution or the solvent (Figure 22.10A), and hence, the freezing point must be lowered to produce the pure solid from the solution because enthalpy of solution formation is zero (Figure 22.10B) but the entropy gap has been reduced.

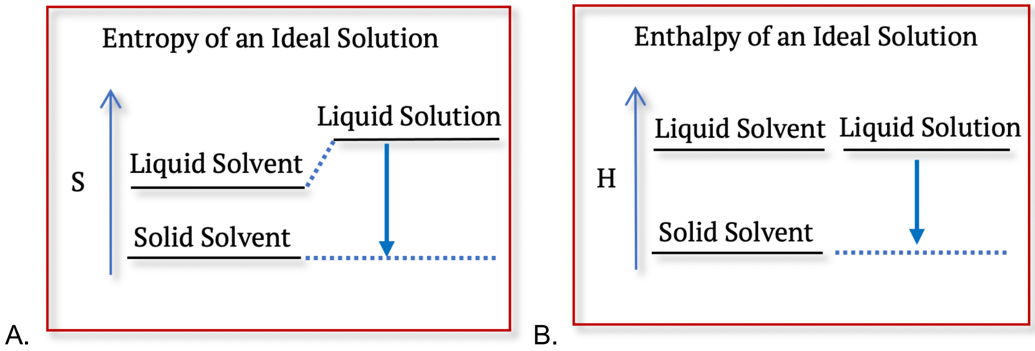

Figure 22.10 The entropies (A) and the enthalpies (B) of the pure solid solvent and liquid solution. The larger entropy gap between the pure solid and the solution requires a lower freezing temperature since ΔH for the solution formation is zero.

Similar explanations can be applied to the process of osmosis where the entropy changes or changes in entropy changes are responsible for the increase in the pressure over the solution.

22.7 Molecular Interpretation

Chemical potential is the basis for the colligative properties, and these are intrinsically at the molecular level and require a knowledge of the molar mass of the solute. At the molecular level, the solute particles replace the solvent molecules and since the solute is chosen to be nonvolatile it suppresses vaporization of the solvent from the solution. Thus, the solution needs to be heated to a higher temperature to bring it to a boil. This is interesting because we assumed that there are no interactions between the solvent and the solute, still the boiling point is elevated. Thus, in addition to the intermolecular interactions contributing to the boiling point of a liquid, there are other contributions such as entropy. The entropic and enthalpic contributions to the phase transitions and how they are influenced by a non-volatile solute are described above. But by far, these properties depend on the number of particles present in the solution, thus providing a direct measure of the molar masses of the dissolved solutes.

22.8 Applications in Daily Life

The colligative properties of solutions are often encountered in daily life and rather common. Throwing salt on snow, for example, melts it away more easily even at 0 ˚C but does not work at much lower temperatures because the salt-ice mixture has a lower melting temperature than ice itself. Indeed, ice-salt mixtures produce lower temperatures than ice points, not discussed here but it is due to the heat of dissolution lowering the temperature. Oceans freeze at a lower temperature than freshwater lakes do because the freezing point of saltwater is less than the ice point. Icebergs contain freshwater because pure water separates when saltwater freezes leaving the salt behind, and the snow that has accumulated on them is due to the freezing of the pure water vapor from the atmosphere in the form of snowflakes. Fish can still survive in cold oceans because it's not completely frozen and saltwater persists below the ice. The fish that live under these conditions lower the freezing point of their blood with specialized anti-freeze proteins. A pinch of salt decreases cooking time as this elevates the boiling point and so, cooking is accelerated due to the higher temperature produced by the solution. The anti-freeze (glycerol-water mixture) has a lower freezing point than water. Such a solution is often used for the de-icing of airplanes before taking off under cold weather conditions.

Figure 22.11 A large reverse osmosis plant in the State of California for converting seawater to freshwater using advanced membranes and high pressure (Wikipedia) See also Figure 22.8B.

The reverse process of osmosis is used on an industrial scale to produce fresh water from it (Figure 22.11). This is being extensively used in California. Reverse osmosis is being used extensively across the world to produce fresh water and forward osmosis is a revolutionary concept that is being developed to make fresh water from seawater at much lower cost than reverse osmosis. In addition, the 21st century is seeing the revival of colligative properties to study and characterize advanced nanomaterials.

22.9 Key points

1. The lowering of the chemical potential when a solute is dissolved spontaneously in a solvent is the underlying reason for the observed colligative properties.
2. The decrease in the chemical potential, in the case of ideal solutions, is due to the increase in entropy of the solute and solvent molecules.
3. The decrease in the chemical potential of the solution requires a higher temperature to boil because the entropy of the solution is higher than the solvent, but enthalpy is the same (ideal behavior, $\Delta H=0$). Thus, the boiling point must be higher to produce the vapor with a smaller entropy increase.
4. The decrease in the chemical potential of the solution requires a lower temperature for the solution to freeze because the entropy of the solution is higher than the pure solid phase of the solvent, but enthalpy is not (ideal behavior). Thus, the freezing temperature must be lower to produce the pure solid with a much larger entropy penalty.
5. Osmosis is the process of pure solvent diffusing spontaneously into the solution across a semipermeable membrane where the membrane allows only the passing of the solvent but not the solute. The chemical potential of the solution is lower than the solvent, and hence, it needs to be under higher pressure to achieve equilibrium with the pure solvent. This excess pressure on the solution is the osmotic pressure.
6. The molar mass of the solute is inversely proportional to the osmotic pressure and this relation can be used to determine the molar masses of molecules and it is recently being used in nanochemistry for the determination of the molar masses of the nanoparticles, with are otherwise difficult to measure.

22.10 Key terms and units

Elevation of the boiling point, lowering of the freezing point, and osmotic pressure. Osmotic pressure (atm).

22.11 Self Reflection

1. Graph the entropy of fusion and entropy of boiling vs T when the corresponding phase transitions occur.
2. Given the space of your dorm room, examine various colligative properties that are being carried out. Discuss at least one of them.
3. Video of a drying salt-water solution spilled on a granite counter in the kitchen appears to evaporate faster in the beginning and become slower and slower with time. Explain why evaporation slows down with time?
4. Discuss the differences and similarities between the ideal and non-ideal solutions.
5. Design corrections to Raoult's law to accommodate repulsive or attractive interactions between the solvent and the solute. Test if your equation can explain the observed behavior of real solutions.
6. Design an experiment to measure the molar masses of nanoparticles that are soluble in a nonpolar solvent.

22.12 Further Reading

1. https://ocw.mit.edu/courses/mechanical-engineering/2-500-desalination-and-water-purification-spring-2009/index.htm2.https://ocw.mit.edu/courses/chemistry/5-111-principles-of-chemical-science-fall-2008/video-lectures/lecture-18/13.6
2. https://ocw.mit.edu/courses/chemistry/5-60-thermodynamics-kinetics-spring-2008/video-lectures/lecture-23-colligative-properties/
3. http://open.uci.edu/lectures/chem_1b_spring_2012_solutions_and_colligative_properties.html

22.13 Self Tests

1. The number of particles of a solute control these properties of solutions

   a. enthalpy

   b. entropy

   c. chemical potential

   d. internal energy

   e. none of these

2. The Raoult's law connects these key variables

   a. the phase transition temperature with ΔS and ΔH of a mixture of non-ideal solutions

   b. the phase transition temperature with ΔS and ΔV of the nonvolatile solvent

   c. the phase transition temperature with ΔS and ΔV of the volatile solute

   d. the vapor pressure with the mole fraction of the nonvolatile solute

   e. none of these

3. The enthalpies of phase transitions control these colligative properties

   a. dissolution of solids in liquids

   b. freezing points

   c. boiling points

   d. both b and c

   e. none of these

4. The boiling point of a pure volatile solvent

   a. increases with solute concentration

   b. decreases with solute concentration

   c. decreases with solvent concentration

d. increases with solvent concentration

e. none of these

5. The increase in the boiling point of volatile solvent in the binary solution

a. increases with the mole fraction of the nonvolatile solute

b. decreases with the mole fraction of the nonvolatile solute

c. increases with the mole fraction of the volatile solvent

d. increases with temperature

e. none of these

6. The following is an example of a colligative property,

a. boiling of water

b. osmosis

c. stone rolling down the hill

d. both a and b

e. none of these

7. The elevation of the boiling point is of a binary solution of a volatile solvent and non-volatile solute is due to

a. the increase in the chemical potential of the solution when compared to that of the pure solvent

b. the decrease in the chemical potential of the solution when compared to that of the pure solvent

c. the equality of the chemical potential of the solution to that of the pure solvent

d. both a and c

e. none of these

8. Colligative properties are useful to measure the following

a. chemical potential of the system

b. enthalpy of the system

c. entropy of the system

d. molar masses of the solutes

e. all of the above

9. Slope of the plot of 1/boiling point on the y-axis and ln (mole fraction of solvent) on the x-axis for a binary solution containing a nonvolatile solvent and volatile solvent is

a. >0

b. <0

c. =0

d. can’t say

e. none of these

10. Slope of the plot of $\Delta T/T$ on the y-axis and mole fraction of the solute on the x-axis for the elevation of the boiling point of a solution containing volatile solvent and a nonvolatile solute is

a. molar enthalpy of vaporization/R

b. <0

c. =0
d. molar entropy
e. none of these

11. The chemical potentials of the solute and the binary solution of a volatile solvent are equal at
    a. the boiling point
    b. freezing point
    c. sublimation point
    d. infinity
    e. none of these
12. In general, the melting point of a solution made of a volatile solvent and a nonvolatile solute is
    a. increases with the mole fraction of the solute
    b. decreases with the mole fraction of the solute
    c. independent of the mole fraction of the solute
    d. decreases with the mole fraction of the solvent
    e. none of these
13. Two nonvolatile solutes can produce the same decrease in the freezing point of a volatile solvent if their
    a. masses are the same
    b. volumes are the same
    c. heats are the same
    d. their molar masses are the same
    e. none of these
14. The chemical potential of salt solution is equal to that of the pure water at pressure equal to
    a. ambient pressure less than the osmotic pressure
    b. ambient pressure/osmotic pressure
    c. osmotic pressure
    d. ambient pressure + osmotic pressure
    e. none of these
15. The osmotic pressure of the salt solution in equilibrium with pure water at room temperature
    a. increases with pressure on the solvent at constant temperature
    b. increases with the mole numbers of the solvent
    c. increases with the mole numbers of the dissolved salt
    d. both a and c
    e. none of these
16. The increase in the boiling point of water containing 0.1 M salt is
    a. 1 K
    b. 0.1 K
    c. 0.01 K

d. 1.1 K

e. none of these

17. The decrease in the melting point of water containing 0.1 M salt is

a. 2 K

b. 0.12 K

c. 0.02 K

d. 2.1 K

e. none of these

18. The decrease in the osmotic pressure of water containing 0.1 M salt is

a. 2 atm

b. 0.12 atm

c. 22 atm

d. 2.1 atm

e. none of these

19. If the freezing point of a solvent containing solute with a mole fraction of 0.1 is decreases from 300 to 297.941 K, the enthalpy of fusion of the pure solvent is

a. 2300 kJ/mol

b. 8.303 kJ/mol

c. 8303 kJ/mol

d. 10000 kJ/mol

e. none of these

20. if the osmotic pressure of a solution is 24 atm at room temperature, the number of moles of a nonvolatile solute dissolved per L of the solution, is

a. 1

b. 100

c. 8.303

d. 2.303

e. none of these

22.14 Self Tests Key

1. e, 2. d, 3. d, 4. e, 5. a, 6. b, 7. b, 8. d, 9. a, 10. e, 11. e, 12. b, 13. e, 14. d, 15. c, 16. e, 17. e, 18. e, 19. c, 20. a

22.15 Problems

1. What is the increase in the boiling point of seawater containing 3.5% salt by weight? (0.31 K)
2. What is the decrease in the melting point of seawater containing 3.5% salt by weight? (Ans. -1.12 K)
3. What is the osmotic pressure exerted by sea water due to 3.5% dissolved salt, at room temperature? (14.74 atm)
4. If a solute of 5% solution in water creates an osmotic pressure of 2 atm under ambient conditions, what is its molar mass? (Ans. 611.6 g/mol)
5. If the freezing point of a solvent containing solute with a mole fraction of 0.1 decreases from 300 to 297.941 K, what is the enthalpy of fusion of the pure solvent? (Ans. 38.03 kJ/mol)

6. If the osmotic pressure of an aqueous solution is 24 atm at room temperature, what are the number of moles of a nonvolatile solute dissolved per L of the solution? (Ans. 0.98 moles)
7. A nanoparticle suspension of 50 g/L exerts an osmotic pressure of 0.5 atm at 300 K, what is the average molar mass of the particles, assuming ideal behavior? (Ans. 2461.7 g/mol)
8. The boiling point of a nanoparticle suspension of 50 g/L is increased by 0.01035 K. What is it average molar mass? (Ans. 2500 g/mol)
9. Nanoparticles of 2500 g/mol were used to make 5% solution in water. What is the change in the freezing point of water at 1 atm? (Ans. -0.0375 K)
10. What is the best colligative property to measure the molar masses of nanoparticles that can be dissolved in a solvent?

Chapter 23. Solutions of volatile solutes and solvents

After completing this chapter, you will be able to:

- Apply Raoult's law to ideal dilute solutions containing only volatile components.
- Relate the mole fractions of the solute in the liquid and vapor phases.
- Apply the concepts of distillations for the separation of soluble components from volatile solutions.
- Distinguish between ideal and non-ideal solutions.
- Recognize the gas-liquid equilibrium and Henry's law.

Goals

- Evaluate the influence of one or more volatile components on the solution properties of a mixture of volatile solvents under ideal conditions.
- Apply Raoult's law to examine the relation between the vapor pressure and the mole fractions of multiple volatile components.
- Discuss the changes in free energy, entropy, and enthalpy of the solvation.
- Examine the properties of non-ideal solutions, fractional distillation and azeotrope formation.
- Apply Henry's law to the gas-liquid equilibrium and quantify gas solubility in liquids.

23.1 Why study this?

Here we will examine the formation of an ideal binary solution from two or more volatile components and examine their solution properties. The fractional distillation and azeotrope formation are key concepts in the practice of chemistry. In addition, the insight gained through the discussions of the chemical potential changes accompanying these phase transitions and deviations from the ideal behavior is useful in designing proper methods for the separation of mixtures. These also feed into our discussions of the molecular descriptions of the forces behind these transitions. The fractional distillations are carried out on an industrial scale in oil refineries to fractionate the crude oil and produce a variety of intermediates to make durable goods needed in our daily lives. Thus, this chapter is of importance in the laboratory and industrial applications of physical chemistry.

23.2 Raoult's law, ∆G and ∆S for Ideal Volatile Solutions

Here, we examine Raoult's law as applied to binary solutions where both the components of the binary solution are volatile as they form an ideal solution at all compositions. This is another example of colligative properties discussed two chapters ago, and most of this chapter follows this theme but deviations from the ideal behavior are also discussed here.

Raoult's law states that the vapor pressure of a volatile component (p_i) dissolved in a volatile solvent is given by its mole fraction (x_i) and the vapor pressure of the pure solvent (p°_i), as given below.

$$p_i = x_i\, p_i^0$$

This is an ideal law, and the situation is similar to the case of the solution containing a nonvolatile solute and a volatile solvent, discussed in the previous chapter. Thus, we simply replace the nonvolatile component with a volatile component and re-examine the properties of the resulting solutions. In the above equation, one could have as many volatile components as one desires and the total vapor pressure will be the sum of the vapor pressures of each of the volatile components p_1, p_2, p_3,…., as given below.

$$p\ (total) = p_1 + p_2 + p_3 + p_4 + \cdots$$

In the above equation, the vapor pressure of the component follows Raoult's law for two volatile components, as outlined earlier. Our discussions will be mostly restricted to solutions of two volatile components and assume that Raoult's Law is valid at all compositions (ideal solutions at all compositions). First, we will build the thermodynamic basis for the formation of ideal solutions, and then construct a framework to explain the basis for the separation of these components from the mixture by fractional distillation.

23.2.1 Thermodynamic conditions for the formation of ideal solutions

Next, we develop the thermodynamic equations for the formation of ideal volatile solutions, as we did in the case of non-volatile solute. Thus, we write the following steps to determine the conditions of ideal behavior, and these steps should be self-explanatory after such detailed derivations of similar equations discussed throughout this book.

$$\mu = \mu^0 + R\,T\ln x_i$$

$$\mu - \mu^0 = R\,T\ln x_i$$

$$\Delta G_{mixing} = n\,R\,T\sum x_i \ln x_i$$

Thus, the Gibbs free energy of mixing is negative, as all quantities in the above equation are positive except the logarithmic term, which is negative. There will be no interactions among particles in an ideal solution, and hence, enthalpy does not contribute to the solution formation.

The entropy term for the dissolution of the solute in the solvent of the ideal solution is from the Gibbs free energy term. We get that by taking the first derivative with respect to the temperature, as follows.

$$\Delta S_{mixing} = -(d\Delta G/dT)$$

$$\Delta S_{mixing} = (d/dT)\left(-n\,R\,T\sum(x_i\ln x_i)\right)$$

$$\Delta S_{mixing} = -n\,R\sum(x_i\ln x_i)$$

Notice that the entropy term will be positive due to the negative sign of the logarithmic terms, because x_i <0, multiplied by the negative sign at the front. All other terms are positive. Thus, the formation of the ideal solution is favored by entropy increases and only due to the entropy. These discussions are summarized in Figure 23.1.

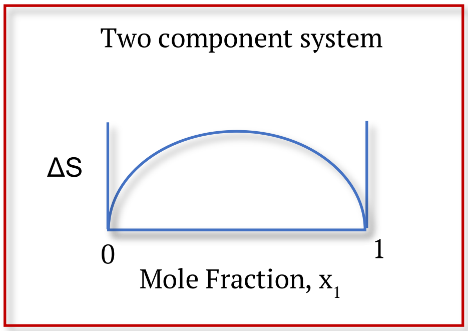

Figure 23.1 Plot of entropy change as a function of the mole fraction of the volatile solute or the solvent, at constant pressure, in an ideal solution. The increase is maximum at 1:1 composition for a binary solution.

Thus, as witnessed before, the entropy of mixing is maximum when the composition is 50:50, and on either side of this, the mixture can still accommodate the other component. Next, we ask what are the enthalpy and volume changes for the formation of the ideal solution?

$$\Delta H_{mixing} = \Delta G_{mixing} + T\,\Delta S_{mixing} = n\,R\,T\sum x_i\ln x_i - n\,R\,T\sum x_i\ln x_i = 0$$

Again, due to the ideal nature of the solution, there are no interactions when the solvent and the solute are mixed, and the enthalpy of solution formation is zero. Then, we conclude that the formation of this ideal solution is entirely driven by a decrease in Gibbs free energy contributed by only entropy increases. Similarly, we arrive at the volume change for the dissolution, as follows.

$$\left(\frac{\partial\Delta G}{\partial p}\right)_{T,n_1,n_2,\dots} = \Delta V_{mixing} = (d/dp)\,(n\,R\,T\sum X_i\ln X_i) = 0$$

Again, since there are no intermolecular interactions, there would be no change in volume as the ideal solution is formed. Thus, the thermodynamic parameters for the ideal solutions made of a volatile solute dissolved in a volatile solvent are the same as in the case of the non-volatile solute dissolved in a volatile solvent. In summary, we have shown that the application of Raoult's law to solutions of two volatile components generated key thermodynamic equations. The spontaneous formation of ideal solutions is driven by the thermodynamic potential due to favorable entropy changes but there are no enthalpy contributions for the solution formation.

Example 23.1

Calculate ΔG, ΔH, ΔV, and ΔS when 1 mol of ethanol is added to 55.5 mol of water at room temperature, assuming ideal behavior.
Ideal behavior, and hence, ΔH = ΔV = 0. ΔS >0, ΔG <0 and these are obtained as following.

$$\Delta G_{\text{mixing}} = \mathrm{n\,R\,T}\sum \mathrm{x_i}\ln \mathrm{x_i}$$

$$= (1+55.5)\,mol\left(8.3144\,L\frac{atm}{K\,mol}\right) * 298.15\,K * \left[\left(\frac{1}{56.5}\right)\ln\left(\frac{1}{56.5}\right)+\left(\frac{55.5}{56.5}\right)\ln\frac{55.5}{56.5}\right] = -12.46\,kJ$$

$\Delta S = -(\Delta G/T)$ = 41.78 kJ/K

23.3 Thermodynamic basis for fractional distillation

We ask the question how does the composition of the vapor differ from that of the solution phase having two volatile components? The answer forms a foundation for the discussions of fractional distillations. If the above two compositions are the same, then the components can't be separated by distillation, because condensing the vapor gives the liquid the same composition as the original mixture. This can happen with an ideal solution only when both components boil at the same temperature. Even if the boiling points are off by a few degrees, we can separate the two components. These details are discussed below as distillation is a very important industrial processes and has significant implications in the laboratory as well.

23.3.1 Total vapor pressure and compositions of the liquid and vapor phases

Next, we investigate how the mole fractions of different components in the liquid influence their compositions in the vapor phase? We recognize that the chemical potentials of both the vapor phase and the liquid phase in the solution are less than their corresponding pure phases, but the compositions in the liquid and the vapor phases need not be the same. We ask, how is the total vapor pressure related to the mole fraction of the solvent and the solute? We begin by writing the chemical potential of the solvent as a function of its mole fraction and then, apply Raoult's law (ideal solution).

$$\mu_1 = \mu_1^0 + R\,T\ln x_1$$

$$p_1 = x_1\,p_1^0$$

Next, we carry out the same analysis for the chemical potential of the volatile solute, as follows.

$$\mu_2 = \mu_2^0 + R\,T\ln x_2$$

$$p_2 = x_2\,p_2^0$$

Using the above two equations, we are on the way to calculating the total vapor pressure of the solution, as given by the following equations.

$$p = p_1 + p_2 = x_1\,p_1^0 + (1-x_1)\,p_2^0$$

$$p = p_2^0 + (p_1^0 - p_2^0)\,x_1$$

Thus, the total vapor pressure (in the absence of inert gas) is the sum of the partial pressures of the vapors of the two components (ideal behavior) and it is linearly related to the mole fraction of the solvent, or it can also be written in terms of the mole fraction of the solute ($x_2 = 1 - x_1$), as shown above.

We predict that the total pressure will be a linear function of the mole fraction of the solvent or the solute. A plot of the total pressure as a function of the mole fraction of the solvent will be linear with a slope equal to $(p_1^0 - p_2^0)$, while the intercepts on either of the two y-axes are as marked in Figure 23. 2.

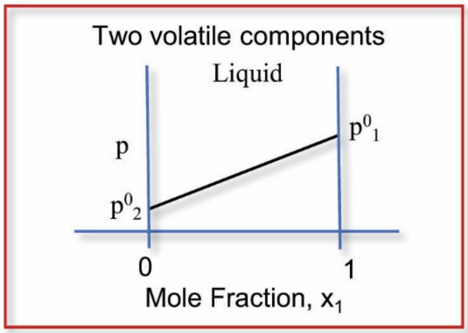

Figure 23.2 Plot of the total vapor pressure of an ideal solution of two volatile components as a function of the mole fraction of the solvent, where the solvent (component 1) is more volatile than volatile solute (component 2).

Example 23.2

What is the total pressure of a solution of a volatile solute in a volatile solvent, if the vapor pressure of the pure solvent is 0.9 atm, and that of the solute is 0.1 atm dissolved at a mole fraction of 0.177? We use the standard equation for ideal solutions to get the total pressure which is directly related to the mole fraction of the solvent. $p = p_2^0 + (p_1^0 - p_2^0)\, x_1$

$$p = 0.1\, atm + (0.9 - 0.1)\, atm\, (1 - 0.177) = 0.886\, atm$$

Thus, the total vapor pressure will depend linearly on the solution composition, for an ideal solution. If the presence of either component influences the vapor pressure of the other, then we expect deviations from the ideal behavior and this is quite common, and the solution no longer follows Raoult's Law.

23.3.2 Total vapor pressure and the composition of the vapor phase

In the above discussions, we examined the dependence of total vapor pressure on the composition in the liquid phase, but we are also interested in knowing how the vapor composition differs from that of the liquid? This is because the condensation of the vapor gives the distillate and thus, its composition of interest in fractional distillation.

The total vapor pressure is a non-linear function of the mole fraction of the solvent and the solute, as shown above. Thus, we have the following steps that are self-explanatory.

$$y_1 = p_1/p$$

Here, y_1 is the mole fraction of the solvent in the vapor phase, which is the partial pressure p_1 divided by the total vapor pressure p. Substituting for the partial pressure of component 1, from the above discussions, we get the next few steps.

$$y_1 = x_1\, p_1^0\, /(p_2^0 + (p_1^0 - p_2^0)\, x_1)$$

$$p = p_2^0 + (p_1^0 - p_2^0)\, x_1$$

$$y_1 = x_1 p_1^0/(p_2^0 + (p_1^0 - p_2^0) x_1$$

Solving for x_1 from the above, we get,

$$x_1 = (y_1\, p_2^0)/(p_1^0 + p_2^0 - p_1^0)\, y_1$$

$$1/p = (y_1/p_1^0) + (y_2/p_2^0)$$

Thus, the inverse of the total pressure is related to the mole fractions of the solvent and the solute in the vapor phase weighted by their corresponding vapor pressures in the pure phases. So, this is a bit more complicated than expected, but a plot of total pressure as a function of the mole fraction of the solute in the vapor phase is shown in Figure 23.3.

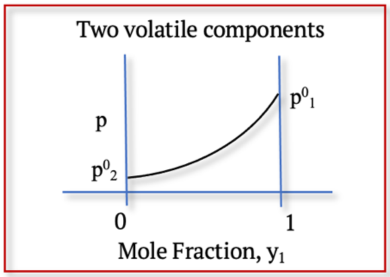

Figure 23.3 Plot of the total pressure of an ideal solution as a function of the mole fraction of the solvent in the vapor phase.

On the left side of the y-axis, when the mole fraction of the pure solvent equals 1, the intercept is the vapor pressure of the pure solvent. From the solute mole fraction from 0 to 1, the total pressure is less than the linear function. That's because the value of total pressure p is dictated by the non-linear composite expression, shown above. A plot of total vapor pressure as a function of the mole fraction in the liquid phase is linear while the plot as a function of the mole fraction in the vapor phase is non-linear. Nevertheless, the vapor composition is now related to total pressure as well as the composition of the liquid and facilitates the discussion of fractional distillation in the next sections.

Example 23.3

The total vapor pressure of a volatile solution is 0.32 atm while the vapor pressure of the pure solvent is 0.7 atm and that of the solute is 0.1 atm. What is the mole fraction of the solute in the vapor phase, if the vapor contains a mole fraction of 0.8 of the solvent?

$$1/p = (y_1/p_1^0) + (y_2/p_2^0) \quad or \quad y_2 = p_2^0\left(\frac{1}{p} - \frac{y_1}{p_1^0}\right) = 0.1\ atm * \left(\frac{1}{0.32\ atm} - \frac{0.8}{0.7\ atm}\right) = 0.2$$

Or we can simply say that the two mole fractions should sum to 1, and hence, solute mole fraction will be 1-0.8 = 0.2 as we got above.

We will discuss an example of the ideal behavior of certain volatile systems, and ask how the compositions of the vapor and the liquid depend on the composition and compare with those of the corresponding pure components?

23.3.3 The benzene-toluene system

Examine the plot of the vapor pressure of the benzene-toluene binary, ideal, volatile solutions as a function of the mole fraction, at constant temperature (Figure 23.4). The plot of the total vapor pressure on the y-axis vs the mole fraction of benzene in the liquid phase on the x-axis gives the red curve. This is a double-Y plot where there are two intercepts on the two axes. When x = 0, mole fraction of benzene is zero, we only have pure toluene, and hence the y-intercept on the left is the vapor pressure of pure toluene.

When the mole fraction of benzene is 1, there is no toluene in the solution, and the vapor pressure is simply due to pure benzene. Thus, the y-intercept on the right equals that of benzene only. The intercept on the right is higher than the one on the left because benzene has a lower boiling point than toluene, and hence it has a higher vapor pressure.

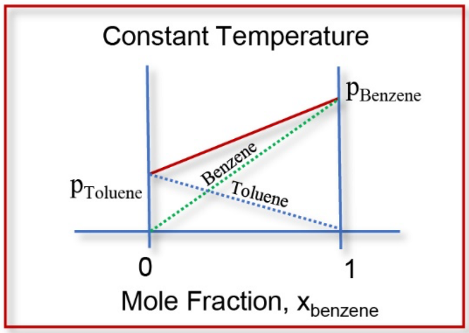

Figure 23.4 The toluene-benzene binary, ideal, volatile component system. The plot of vapor pressure vs the mole fraction of benzene.

Therefore, the red line connecting these two extreme points is straight and that's due to the ideal behavior of mixtures with mole fractions between 0 and 1. The plot is linear due to its ideal behavior obeying Raoult's law. The green dotted line shows the contribution of the vapor pressure of benzene to the total vapor pressure of the mixture.

Similarly, the contributions of the vapor pressure of toluene to the total vapor pressure are given by the blue dotted line, and the sums of the vapor pressures of that of benzene and due to toluene add up to that of the total mixture (red line). Thus, the total vapor pressure is linearly dependent on the mole fractions of the two volatile liquid components. Deviations from the ideal behavior will be observed as deviations from the linear plots, and as we saw before, these could be positive or negative deviations.

Example 23.4

Vapor pressure of pure benzene is 75 mm Hg and that of toluene is 22 mm Hg, at 20 ˚C. If the mole fraction of toluene in the vapor is 0.1 what is the total vapor pressure?

$$1/p = (y_1/p_1^0) + (y_2/p_2^0) \quad or\ p = \frac{1}{(y_1/p_1^0) + (y_2/p_2^0)} = \frac{1}{(\frac{0.1 * 760\ mm\ Hg}{22\ mm\ Hg} + \frac{0.9 * 760\ mm\ Hg}{75\ mm\ Hg}} = 0.08\ atm$$

The total vapor pressure of a volatile solution is 0.5 atm while the vapor pressure of the pure solvent is 0.7 atm and that of the solute is 0.1 atm.

in summary, the ideal behavior of binary volatile solutions is that they behave as if they are the same substance but with two distinct boiling points and can be fully separated from each other. The vapor pressure of the mixture is the sum of the vapor pressures of the two pure components. Raoult's law is obeyed by both the components at all compositions and the two components behave as if they do not recognize the presence of the other.

23.4 Isothermal Fractional Distillation

Since the vapor pressure of a volatile component is a function of external pressure applied on the liquid, we surmise that the vapor pressure of a mixture of volatile components will also depend on the external pressure. We will now examine the effect of pressure on the composition of the vapor and the liquid phases of an ideal, binary solution of two volatile liquids. As the pressure is reduced at a constant temperature, the chemical potential of each component decreases both in the vapor and the liquid phases. The extent of the decrease depends on the molar volume of the component defined by $d\mu = V_{molar}\ dp$ for each component, at constant temperature ($dT = 0$). So, some components will respond more rapidly to a decrease in pressure than the others, in accordance with their molar volumes. We will construct pressure-composition diagrams to understand the changes in the composition as a function of pressure and form a basis for isothermal distillation under reduced pressure.

23.4.1 Vapor composition of a volatile mixture as a function of pressure at a constant temperature

Consider Figure 23.5 where the pressure on the y-axis is plotted as a function of the mole fraction of component 1. The liquid phases dominate at higher pressures and the vapor phase dominates at lower pressure. These diagrams have two y-axis intercepts, and on the right $x_1 = 0$, and hence, the intercept corresponds to the vapor pressure of pure component 2 or p°_2. On the right y-axis, the intercept is the vapor pressure of the pure component 1 ($x_1 = 1$) at p°_1. Anywhere in-between the x_1 values of 0 and 1, the mole fractions of components 1 and 2 are changing continuously.

The red line separates the liquid phase from the liquid-vapor mixture and the blue curved line separates the vapor from the liquid-vapor mixture, while the area enclosed in the bowl bordered by the red and the blue lines is where the liquid and vapor co-exist at all compositions.

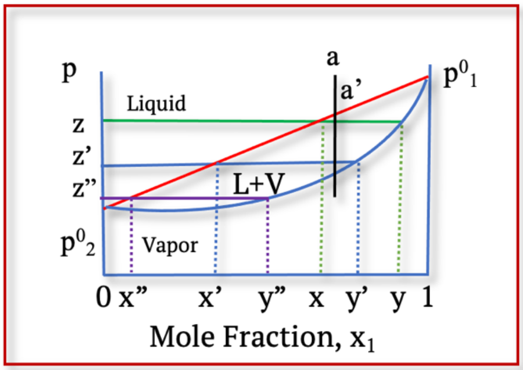

Figure 23.5 Plot of the total pressure of an ideal solution of two volatile components as a function of the mole fraction of the solvent, where the solvent has a lower boiling point or higher vapor pressure than the solute.

At any given pressure, we draw a line horizontal to the x-axis and read off the composition of the liquid or the vapor phase from these diagrams, as indicated by the green, blue and purple horizontal lines. At pressures z, z' and z", the corresponding compositions of the vapor in equilibrium with the liquid (blue curved line) are y, y', and y", respectively. Thus, as we change the pressure, the composition of the vapor is changing because the most volatile phase is richer in the vapor phase while the less volatile one is enriched in the liquid phase.

From the above plot, the compositions of the liquid/vapor phases can also be read off. For example, if we start with a mixture with composition 'a' (top of the black vertical line) and reduce the pressure on the mixture, the first vapors will begin to appear at pressure a' and if we continue to lower the pressure to z, the liquid phase will have a composition of x, and vapor composition of y. Further pressure drop to z', liquid is of composition x', while the vapor composition changes to y'. Reducing the pressure further down to Z'', the vapor will have a composition of y'', while the liquid will have a composition of x''.

These horizontal lines give the exact composition of the vapor and the liquid at a specific pressure. As we lower the pressure, the compositions are changing in both the liquid and the vapor phases, and the liquid composition moves along the red slanted line while the vapor composition moves along the blue curved line. If we repeat the distillation with any of these condensates, they will be further enriched in the more volatile component and by repeating this process several times, a pure component can be obtained as the condensate.

Similarly, if we re-distill the leftover liquid, it will continue to enrich the less volatile component (composition changes to the left), and ultimately, we will have the pure component 2 or the less volatile component in the pot after several re-distillations.

In simple terms, the red line represents the composition of the liquid phase and the corresponding pressure where the less volatile component exists in the liquid phase, and the red line is the liquid-vapor equilibrium boundary. Above the red line, only the liquid phase exists. Similarly, the blue line in the bottom is the vapor-liquid line where the vapor is in equilibrium with the liquid, and only vapor exists below the blue line.

Example 23.5

The composition of most wines is about 11% ethanol or a mole fraction of 0.0461, remaining being water. What is the change in the chemical potential of ethanol and that of water in such a typical wine with respect to the standard chemical potentials of pure alcohol and pure water in their liquid phases at 300 K?

$\mu_j(\text{liquid}) = \mu_j^*(\text{liquid}) + \mathrm{R\,T} \ln x_j$ $\Delta\mu(water) = R\,T\,lnx_{water} = 8.3144 \frac{J}{K\,mol} * 300\,K \ln(1 - 0.0461) = -117.8 \frac{J}{mol}$. Similarly, change in the chemical potential of alcohol is -7.673 J/mol. The minor component had much lower chemical potential than the major component, an important consequence of mixing.

In summary, the effect of decreasing pressure on the composition of the vapor is that the vapor phase is enriched in the more volatile component, while the liquid phase is enriched in the less volatile component. The pressure-composition diagrams, thus, show a path to separate the components of mixtures of volatile components at a constant temperature, and they are most suitable for substances that are sensitive to temperature. These are not commonly employed due to the difficulty of varying the pressure to capture the distillates. Instead, varying the temperature at constant pressure is a good alternative, works on a similar principle discussed below.

23.5 Isobaric Fractional Distillation

We will examine the effect of temperature on the vapor pressures of the volatile components of a binary ideal solution at constant pressure. Isobaric distillation is like the isothermal distillation that we discussed earlier. Since the two liquids generally have different boiling points or volatilities, we expect that the composition in the liquid phase differs from that in the vapor phase. As we raise or lower the temperature, these compositions will also get adjusted accordingly. We ask as we change the temperature, will the vapor or the liquid phase be enriched in one of the two components more than their initial composition? The basis for this thought is that the chemical potentials of the vapor and the liquid phases of each component are a function of temperature, but the dependencies are determined by the molar entropies of the components ($d\mu = -S_{molar}dT$) at constant pressure ($dp=0$). Based on this, the chemical potentials of the liquid and the vapor phases of one component are quite different from those of the other component.

The temperature-composition diagrams are generally produced experimentally by determining the compositions of the liquid and vapor phases at a variety of temperatures while holding pressure at 1 atm. So, we ask the question, do the vapor and liquid differ in their compositions at different temperatures? Two separate cases can be considered for the convenience of our discussion.

23.5.1 Case 1: Solvent is more volatile than solute

First, consider the binary ideal mixture of two volatile components where component 1 is more volatile than component 2 and hence, component 1 will have a lower boiling point than component 2. As the mole fraction of component 1 increases on the x-axis from the left to the right, we expect that the intercept on the right y-axis will be the boiling point of pure component 1. Similarly, the left y-intercept will the boiling point of the pure component 2, and this will be larger than that of component 1 (Figure 23.6).

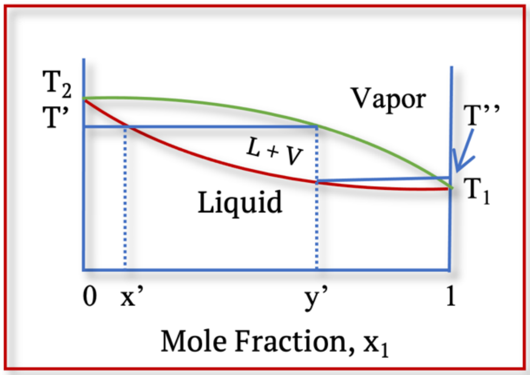

Figure 23.6 Plot of the boiling point of an ideal solution of two volatile components as a function of the mole fraction of the solvent (x_1) where the solvent has a lower boiling point or more volatile than the solute.

The green line represents the composition of the vapor-liquid boundary, while the red line corresponds to the liquid-vapor boundary. Since the y-axis is temperature, only the vapor exists at higher temperatures while only the liquid exists at lower temperatures. The region enclosed by the red and the green lines is where both the vapor and the liquid coexist in equilibrium.

At any temperature T’, we can read off the composition of the liquid and the vapor phases. At T’ for example, the horizontal line drawn parallel to the x-axis (black line) has the intercept at x’ on the x-axis. This is the composition of the liquid phase at that temperature which is in equilibrium with the vapor. The vapor composition, however, is different at this temperature. It’s given by the blue dotted line that intersects the purple and the green lines at y’. So, this is the beauty of the system because a given substance has different chemical potentials in the vapor and the liquid phases, and different substances have different chemical potentials. In any given phase, they have different compositions as a function of temperature. This is the basis for the isobaric fractional distillation.

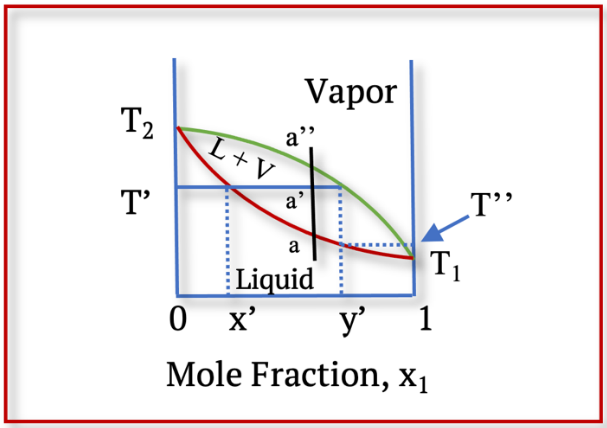

Figure 23.7 Separation of a lower boiling or more volatile component from a higher boiling component by fractional distillation at constant pressure.

If we begin with a mixture of composition a, and raise the temperature, it will begin to boil, and as it boils its composition keeps changing and the boiling point continues to increase (Figure 23.7). If we collect the vapors at a certain temperature T’ and condense and analyze them, they will have a composition given by y’. The liquid composition would have shifted from a to x’ or enriched in component 2 or lost some of component 1. Since y’ is further to the right than a, the condensate will be enriched in component 1, the more volatile component. Thus, the composition of the liquid changes as we boil off a certain amount of component 1, and when we boil the condensate of composition y’, we get vapors that are further richer in component 1 and the boiling occurs at T”. Thus, ultimately, by distilling, condensing, and re-distilling the condensate, we gradually enrich the vapor with the more volatile component while the liquid gets enriched in the less volatile component.

23.5.2 Case 2: Solvent is less volatile than solute

We now examine the case where component 1 is less volatile or has a higher boiling point (Figure 23.8) and $T_1>T_2$ where T_1 is the boiling point of component 1 and T_2 is the boiling point of component 2. This is essentially the same as the previous figure except that the y-intercept on the right is moved to the left and that on the left was moved to the right. If we start with a liquid composition at ‘a’ and heat, it begins to boil at temperature a’ and the composition of the liquid keeps changing along the blue curved line as its boiling point increases. If we now collect vapors at the temperature T’ and condense them to a liquid, it will have a composition of y’ while the liquid that is left in the pot will have a composition of x’. Thus, we enriched the vapors in the more volatile component 2 and the liquid with the less volatile component 1. Thus, a repeat of the distillation with either fraction will continue to enrich the two components at each step.

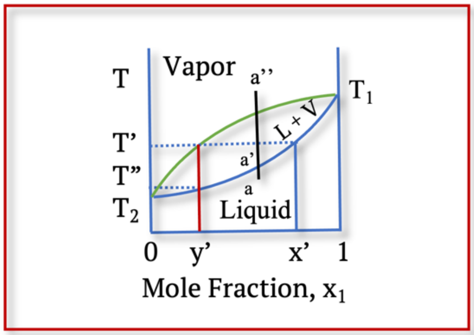

Figure 23.8 Separation of a lower boiling component 2 from a higher boiling component 1 by isobaric fractional distillation.

In summary, the effect of increasing the temperature on a mixture of volatile components is that the composition of the vapor and the liquid phases change as the boiling occurs with a concurrent change in the composition of the liquid. Thus, the boiling point keeps rising as the liquid is enriched in a less volatile component while the vapor phase is enriched with the more volatile component. Thus, the isobaric distillation is used to separate the mixtures of two or more volatile components by repeated distillation and condensation steps.

23.6 Non-ideal Solutions and Azeotropes

Strong molecular interactions between the solute and the solvent can result in deviations from ideal behavior. They may form non-ideal solutions and this behavior could result in the formation of solvent-solute complexes at a fixed composition called azeotropes, and these mixtures boil at a constant temperature without a change in composition. That is, the vapor and the liquid phases of an azeotrope have the same composition, even though they have two or more different chemical components without forming a chemical compound. Azeotrope is a physical complex that is stable at its boiling point. The formation of such azeotropes has a significant impact on the distillation of the corresponding components. Azeotropes often have a boiling point of their own, which can be less than either volatile component (negative azeotrope) or a higher boiling point (positive azeotrope). Because the azeotrope distills at constant composition, the underlying components can't be separated by distillation. These details are discussed next.

23.6.1 Negative azeotropes

The temperature-composition diagram of a typical two-component, negative azeotrope is shown in Figure 23.9. On the x-axis, as usual, is the mole fraction of one of the two components that form the azeotrope, and the leftmost value is zero while the right-most value is 1, for component 1. The two y-axis intercepts are the corresponding temperatures where the right axis gives the boiling point of the pure component 1, while the left intercept is the boiling point of component 2. Until now, this description is like that of the others we have discussed so far.

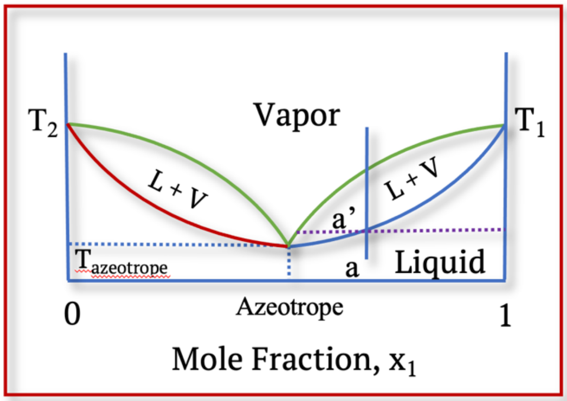

Figure 23.9 Separation of a lower boiling component from a higher boiling component by fractional distillation where a lower boiling negative azeotrope is formed.

The diagram can be divided into the right of the minimum and left of the minimum, and each half shows the usual temperature composition diagram where one of them is the azeotrope and the other is one of the two components. Thus, using this approach, each half can be readily explained in terms of the composition of one of the components and that of the azeotrope. For example, on the left side of the plot, the mixture boils at any composition where the vapor is enriched in the azeotrope while the liquid is enriched in component 1, and we do not see pure component 2 in the vapor phase.

A different situation occurs on the right side of the minimum, and the vapor is still enriched in the azeotrope but the liquid phase is enriched in component 2 because component 2 boils at a higher temperature than the azeotrope itself. Thus, by distillation one of the two components can be separated from the azeotrope but a complete separation of the two components is not possible.

These discussions are more clearly illustrated in Figure 23.9, where at any composition a in the liquid phase, the vapor phase will have a composition of azeotrope given by x', in equilibrium with the liquid phase. Thus, fractional distillation will eventually result in the separation of the azeotrope from the mixture and the enrichment of the liquid in component 2.

23.6.2 Positive azeotropes

Analogously, one also observes a situation where the azeotrope boils at a temperature that is higher than either of the two components. The maximum temperature is at the composition of the azeotrope, or the formation of a positive azeotrope (Figure 23.10). The fractional distillation of the mixture will enrich one of the two components in the vapor, depending on which side of the azeotrope we start, while the liquid gets enriched with the azeotrope, regardless.

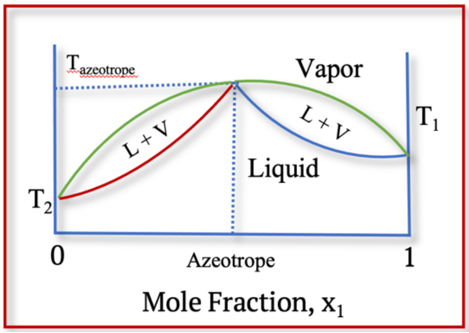

Figure 23.10 Separation of a lower boiling component from a higher boiling component by fractional distillation where a higher boiling positive azeotrope is formed.

In summary, certain non-ideal liquid-liquid mixtures can be separated into the less volatile component and an azeotrope, and the azeotrope distils without a change in its composition and a finite boiling point different from either of the two components. Hence, the azeotrope can't be completely separated further into its components. A different approach is needed to separate azeotropes. The deviations from the ideal behavior at the fundamental level are the reason the azeotropes are formed.

23.7 Gas-Liquid Solutions and Henry's Law

Gases dissolve in liquids, and these are of high importance in industry, environment, and biology. For example, the entire beverage industry depends on gas-liquid solutions, and the dissolution of increased amounts of carbon dioxide due to greenhouse gas emissions are affecting the coral populations, a major environmental issue. Gas-liquid solutions are important in photosynthesis, the most important photoreaction on the planet. The transport of oxygen and carbon dioxide in biological systems is another example of gas-liquid solutions, again on a very large scale on this planet. Thus, discussion of this fundamental process is central to our understanding of solutions and their behavior.

Example 23.6

Calculate ΔG, ΔH, ΔV and ΔS, when a gas of 1 mol dissolves completely in 50 mol of water at 200 K and 1 atm pressure, in a closed container, assume ideal behavior.

$$\Delta G = n\,R\,T \sum x_i \ln x_i = (50+1)\ mol * 8.3144 \frac{J}{K\ mol} * 200\ K \left(\left(\frac{50}{51}\right)\ln\left(\frac{50}{51}\right) + \left(\frac{1}{51}\right)\ln\left(\frac{1}{51}\right)\right) = -8.2\ kJ$$

$\Delta S = -(\Delta G/T)$ = 40.9 J/K; ideal solution has ΔH=0 and ΔV=0 as well.

To an approximation, the gas-liquid solutions can be treated as ideal solutions obeyed by another ideal law, Henry's law. We recognize that this is not universal and recall that a solution of HCl in water is far from being an ideal solution. When the interactions between the gas and the liquid are weak, an ideal solution can be formed and such a solution, under dilute conditions obeys Henry's law. We will examine the chemical potentials of both the solute and solvent to examine the properties of the resulting solutions as presented below.

Let j-components of different gases dissolve in a liquid and attain equilibrium. Then, the chemical potentials of the jth component in the liquid phase are equal to that of the same component in the gas phase, and we can write the following equation to express the equilibrium in terms of their chemical potentials.

$$\mu_j(\text{liquid}) = \mu_j(\text{gas})$$

We express the chemical potential of the gas at the pressure p_j in terms of its chemical potential at 1 atm, as below.

$$\mu_j(\text{liquid}) = \mu_j^0(\text{gas}) + R\,T \ln p_j$$

Henry's law states that the solubility C_j of the jth component is linearly related to its partial pressure, as $K_j\, p_j = C_j$ with the proportionality constant K_j. Now, substituting for p_j in the above equation, we get the following in terms of K_j. A plot of the gas pressure of the jth component as a function of concentration in the liquid phase is shown in Figure 23. 11.

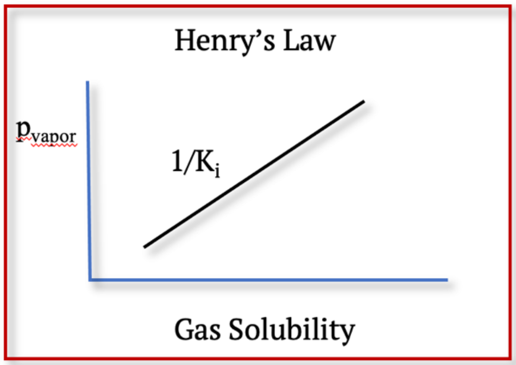

Figure 23.11 Plot of the partial pressure of a gas over the liquid as a function of its solubility in the liquid phase is linear (ideal behavior) and the slope is equal to $1/K_j$.

Table 23. 1 Henry's Law constants under ambient conditions

Compound	*Formula*	*K_j (mol/L atm) x10^3*

Argon	Ar	1.4
Carbon Monoxide	CO	0.95
Carbon dioxide	CO_2	34
Helium	He	0.37
Hydrogen	H_2	0.78
Nitrogen	N_2	0.61
Oxygen	O_2	1.3

Example 23.7

Calculate the mole fraction of carbon dioxide, if its partial pressure is 0.0003 atm in a typical carbonated beverage? (K_j = 0.034 mol/L atm)

$$K_j\, p_j = C_j \;= 0.034 \frac{mol}{L\; atm} * 0.0003\; atm = 1.2\text{x}10^{-5} \text{ mol/L}$$

Non-ideal solutions of gases have enthalpy of solubilization which is a function of temperature, and solubilities of these gases depend on the temperature. For ideal solutions, the enthalpy of solubilization is zero but for real solutions, the temperature dependence of $\Delta H_{solubility}$ is given by the van 't Hoff equation, over a short temperature range when enthalpy is nearly independent of temperature. The solubility of oxygen in water decreases with increase in temperature, cooler waters dissolving more of this gas.

$$\frac{d\; lnH}{d\left(\frac{1}{T}\right)} = \frac{-\Delta H_{solubility}}{R} \quad or \quad H_2 = H_1 \exp[\frac{-\Delta H_{solubility}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)]$$

In summary, Henry's law ($K_j\, p_j = C_j$) is applied to estimate the solubilities of gases in liquids by knowing their partial pressures over the solution and the corresponding Henry's constant. The solubility is directly proportional to the partial pressure of the gaseous component as well as the nature of the solvent. Henry's constants for a few gases are given in Table 23.1.

23.8 Molecular Interpretation

The molecular level explanation for the ideal behavior of solutions is based on the similarities of interactions between the solvent-solvent, solute-solute, and solute-solvent interactions. When these are the same or nearly the same, then they do not distinguish each other and behave as if it is the same fluid throughout the sample. Then, the vapor pressures will scale linearly with the mole fractions of the components of the solution or obey Raoult's law.

An ideal solution is formed when the solute-solute and solvent-solvent interactions are identical. This only happens in a mixture of ideal gases or ideal solvents. When a solute molecule is surrounded by solvent molecules, there is no distinction between one molecule versus its neighbor in terms of intermolecular interactions, even though you have molecules of A dissolved in molecules of B. The idea being that molecules of A don't see the molecules of B as different, and molecules of B don't see those of A as different, and they behave as if they are all the same. Such components follow ideal solution behavior and can be separated by distillation.

However, when the intermolecular interactions among the component molecules are significantly different, then some interactions will be stronger, some will be weaker or some could be even repulsive, resulting in deviations from the ideal behavior. Then, the molecules of one component recognize and interact with the molecules of other components differently from their own, and the behavior deviates from Raoult's law.

23.9 Applications in daily Life

Raoult's law is applied in many of our daily production of industrial goods and encountered in the laboratories, extensively. Fractional distillation of complex mixtures of liquids is a large, industrial process. An example is the oil refineries across the world that process crude oil. Crude oil has a variety of hydrocarbons, many of which are volatile components, as a complex mixture. This is fractionated into a variety of industrial products of high price and utility by fractional distillation and one of the major examples of the applications of distillation. The distillation of crude oil is carried out under constant pressure conditions used in giant refineries and the components are separated by the differences in their boiling points.

Another major example of fractional distillation is the separation of ethanol from the fermented broths of grapes or/and other fruits by the beverage industry. The components are separated using the same principle that one liquid has a certain boiling point, the other liquid has a higher or a lower boiling point, and the mixture is separated by temperature-based fractional distillation.

Henry's law is applied under many situations in daily life as well. Take the example of oxygen and water. The dissolution of oxygen in water is essential for breathing and its use in our metabolism. The dissolved oxygen in water is complexed with hemoglobin and circulated the body in the red blood cells. Similarly, the dissolution of carbon dioxide and its transport is another example of gas-liquid solutions. These do not obey Henry's law exactly and deviate from the ideal behavior due to the formation of finite chemical entities with proteins and other components in the biological systems. When oxygen is bubbled through the water of an aquarium, a certain amount of oxygen dissolved in the water reaches a certain equilibrium upon saturation and the fish can uptake the dissolved oxygen for their metabolic processing. We can say that the chemical potential of oxygen in the water phase is less than that of the chemical potential of oxygen molecules in the gas phase.

The beverage industry of soft drinks also uses Henry's law extensively, where carbon dioxide is dissolved in water under higher than atmospheric pressure. When a bottle of cola bottle is opened or a champagne bottle is open, the internal pressure of the bottle is reduced to that of the atmosphere, and consequently, the dissolved carbon dioxide is released due to the dynamic equilibrium between the dissolved gas and the gas above it. This results in the fizzy foam that forms when the bottle is opened.

23.10 Key points

1. The ideal binary and multi-component volatile solutions obey Raoult's law. $p_i = x_i\, p_i^0$
2. Conditions of ideal behavior are ΔH=0; ΔV=0; ΔS >0; ΔG<0. $\Delta G_{mixing} = n\, R\, T\, \sum x_i \ln x_i$ $\Delta S_{mixing} = -\, n\, R\, \sum(x_i \ln x_i)$ $p_2 = x_2\, p_2^0$ $p = p_2^0 + (p_1^0 - p_2^0)\, x_1$
3. Deviations from ideal behavior can be positive or negative due to interparticle interactions.
4. The formation of chemically stable complexes between the solvent and the solute can result in azeotropes that distill without change in their composition, constant boiling point.
5. Azeotropes deviate from the ideal behavior with a higher boiling point than either component, or a lower boiling point than either component.
6. Henry's law can be used to model the gas-liquid solutions, as an ideal law and of importance in many applications, including the beverage industry.

23.11 Key terms and units

Raoult's Law; chemical potential; positive and negative azeotropes; Henry's law. The terms discussed here are already presented in the previous chapters. In addition to the above equations, we also have:

$$1/p = (y_1/p_1^0) + (y_2/p_2^0) \qquad \mu_j^*(\mathrm{liquid}) = \mu_j^0(\mathrm{gas}) + \mathrm{R\,T} \ln \mathrm{K_j} \qquad \mu_j(\mathrm{liquid}) = \mu_j^*(\mathrm{liquid}) + \mathrm{R\,T} \ln \mathrm{x_j}$$

$$K_j\, p_j = C_j \qquad H_2 = H_1 \exp[\frac{-\Delta H_{solubility}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)]$$

23.12 Self Reflection

1. Plot vapor pressure vs composition for a binary non-ideal, solutions of volatile components.
2. plot chemical potential vs composition for a binary, ideal, solution of volatile components.
3. plot the boiling point vs composition for an ideal, binary, solution of volatile components. Explain the concept of steam distillation, being used in the perfume industry, on molecular terms.
4. Propose corrections for Raoult's law for real solutions since ideal solutions are formed when solvent-solvent interactions are identical to solute-solute interactions and add correction terms based on experimental parameters.
5. Correct for deviations from Henry's law by expanding the equation as a power series and discuss how you would measure specific constants introduced in the new equation. Test your equation with data from the internet.
6. Plot vapor pressure vs composition for binary non-ideal solutions of volatile components; plot chemical potential vs composition for a binary, ideal, solution of volatile components.

7. Plot the boiling point vs composition for an ideal, binary, solution of volatile components.
8. Imagine that you landed on a new planet where there is no liquid water but there is plenty of water vapor, and the temperature is below the critical point of water. How do you plan to extract liquid water from the atmosphere without cooling?

23.13 Further Reading

1. https://ocw.mit.edu/courses/chemistry/5-60-thermodynamics-kinetics-spring-2008/video-lectures/lecture-21-ideal-solutions/
2. https://ocw.mit.edu/courses/chemistry/5-60-thermodynamics-kinetics-spring-2008/video-lectures/lecture-22-non-ideal-solutions/
3. http://www.chemistry2011.org/ResourceFiles/5_60_lecture22.pdf

23.10 Self Tests

1. When two volatile liquids form an ideal solution, we have

   a. a liquid-liquid solution

   b. a liquid-gas solution

   c. a gas-gas solution

   d. all the above

   e. none of these

2. The ideal binary solutions of two volatile liquids obey

   a. the ideal gas law

   b. the Raoult's law

   c. the Henry's law

   d. both b and c

   e. none of the above

3. The enthalpies of formation of the binary, ideal, solutions from volatile components are

   a. >0

   b. <0

   c. =0

   d. can be all the above

   e. none of these

4. The Raoult's law states that the

   a. enthalpy increases with temperature, at constant pressure

   b. enthalpy decreases with temperature, at constant pressure

   c. enthalpy decreases with pressure, at constant temperature

   d. enthalpy increases with pressure with increase in temperature

   e. none of these

5. The vapor pressure of the solvent of an ideal, binary solution of two volatile solvents

   a. is directly proportional to its mole fraction in the liquid phase

   b. is directly proportional to its mole fraction in the vapor phase

   c. is inversely proportional to its mole fraction in the liquid phase

   d. is proportional to its mole fraction in the liquid phase and the gas phase combined

e. none of these

6. The following is an example of a phase transition,

a. evaporation of a solvent from its solution

b. the decomposition of lime stone

c. stone rolling down the hill

d. evaporation of a nonvolatile solute from its solution

e. none of these

7. The volume change accompanying the formation of an ideal solution of 2 or more components is

a. >0

b. <0

c. $=0$

d. both a and b

e. none of these

8. When a liquid boils to vapor, spontaneously, the following decreases

a. chemical potential of the system

b. enthalpy of the system

c. entropy of the system and the surroundings

d. both a and c

e. all of the above

9. The plot of ΔS on the y-axis and mole fraction on the x-axis for an ideal binary solution has a

a. maximum at some random composition for highest entropy change

b. maximum at 1:1 composition

c. maximum when only one component is present

d. can't say

e. none of these

10. Slope of the plot of total vapor pressure on the y-axis and the composition on the x-axis for an ideal, binary, volatile, liquid-in-liquid solutions is

a. molar volume

b. <0

c. $=0$

d. molar entropy

e. none of these

11. Plot of the total vapor pressure vs the liquid composition of a binary, ideal, volatile liquid-liquid solution is

a. linear

b. with a positive slope

c. linear with a negative slope

d. curved but the slope can be positive or negative

e. none of these

12. In general, the molar entropy of a binary solution of ideal, volatile components is

a. greater than the vapor but less than the liquid

b. greater than that of the liquid but less than molar entropy of the vapor

c. greater than that of the vapor but less than the molar entropy of the liquid

d. less than either that of the liquid or the vapor but not both

e. none of these

13. Plot of the total vapor pressure as a function of mole fraction of the solvent in the vapor phase is

a. linear

b. linear but with positive slope

c. linear but with negative slope

d. can't say

e. none of these

14. The slope of the plot of total vapor pressure as a function of the mole fraction of volatile solute and volatile solvent in an ideal solution is

a. positive

b. negative

c. positive or negative

d. neither positive nor negative

e. none of these

15. The fractional temperature-dependent distillation is based on the fact that

a. vapor pressure increases with pressure at constant temperature

b. vapor decreases with pressure at constant volume

c. vapor pressure increases with mole numbers

d. both a and c

e. none of these

16. The component with a lower boiling point in a binary, ideal, volatile mixture has

a. higher vapor pressure than the other component

b. lower vapor pressure than the other component

c. vapor pressure the same as the other component

d. can't say

e. none of these

17. An azeotrope is a mixture of components that have

a. a constant boiling point

b. a constant composition in the liquid and vapor phases

c. boiling point where the composition of the liquid does not change

d. all the above

e. none of these

18. The total vapor pressure of an ideal binary solution of volatile components is

a. the ratio of one vapor pressure to that of the other

b. a linear combination of the vapor pressures of the pure components

c. a difference in the vapor pressures of the pure components

d. can't say

e. none of these

19. The Henry's law states that the partial pressure of a gas above a liquid is proportional to its

a. concentration in the liquid phase

b. mole fraction in the liquid phase

c. mole fraction in the gas phase

d. a combination of concentrations in the liquid and the gas phases

e. none of these

20. The chemical potential of a gas in an ideal gas-liquid solution

a. exponentially increases with its partial pressure

b. exponentially decreases with increase in its mole fraction

c. decreases linearly

d. increases linearly

e. none of these

23.15 Self Tests Key

1. d, 2. d, 3. c, 4. e, 5. a, 6. a, 7. c, 8. a, 9. b, 10. e, 11. d, 12. e, 13. e, 14. c, 15. e, 16. b, 17. d, 18. b, 19. c, 20. b

23.16 Problems

1. A volatile solute was added to water with an increase in the entropy of the system by as much as 12.5 J/K, under ambient conditions. If the solution is ideal, what are the mole fraction of the solute? What is ΔG? (Ans. 0.0042, -3.7 kJ/mol)
2. What is the mole numbers of the volatile solute if the total pressure of a solution of a volatile solute in a volatile solvent is 0.823 atm, if the vapor pressure of the pure solvent is 0.9 atm, and that of the solute is 0.1 atm? (Ans. 5.6 mol)
3. What is the total pressure if a volatile solution is made of a volatile solvent and solute, and the vapor pressure of the pure solvent is 0.3 atm, and that of the pure solute is 0.1 atm at a solute vapor mole fraction of 0.23? (Ans. 0.214 atm)
4. Table wines contain about 11% of ethanol (vapor pressure of pure ethanol = 0.08 atm at 25 ˚C) by weight, rest being water (vapor pressure of pure water 23.8 torr at 25 ˚C). What is the vapor pressure of ethanol and total vapor pressure in a bottle of wine that is half empty but closed at 25˚C? (Ans. 0.0037 atm, 0.034 atm)
5. Design an experiment to separate alcohol from its aqueous solution.
6. What are ΔG and ΔS when an ideal solution of equal moles of solute and solvent are formed? (Ans. -3.5 kJ/mol and 11.5 J/K mol)
7. The Henry's law constant for the dissolution of oxygen in water is 0.0013 mol/L atm at room temperature. What is oxygen concentration is surface waters on the planet? (Ans. 0.27 mmol/L)
8. Solubility of oxygen in water decreases with increase in the temperature. Discuss the effect of global warming on the aquatic life, just from this one factor.

9. The global carbon dioxide level is presently 412 ppm. What is its partial pressure in mm Hg and in atm? Given its Henry's constant of 0.034 mol/L atm, what is the concentration dissolved in water? (Ans. 0.3 mm Hg, 0.000412 atm, 0. 14 μM)
10. The global levels of carbon dioxide are projected to increase to 685 ppm by 2050, what will be the concentration of dissolved CO_2 in the oceans by then? (Ans. 201.7 μmol/L)